Volume XXII. *April, 1906.* *Number 4.*

THE

PHYSICAL REVIEW.

THE PHENOMENA OF IONIZATION IN FLAME GASES AND VAPORS.[1]

By F. L. Tufts.

Introduction.

In a previous paper on the phenomena of ionization in flames[2] the writer described a new method for studying the phenomena of electrical conduction through flame gases and vapors. The old method, employed by Sv. Arrhenius,[3] H. A. Wilson[4] and most other investigators of the electrical conductivity of flames, was to introduce into the flame under investigation clean platinum electrodes which became heated to incandescence by the flame. The conductivities of the flame gases and vapors between the electrodes were then compared by comparing the currents which a given impressed electromotive force would send through the flame.

All investigators found that under the above conditions the current increased less rapidly than the impressed electromotive force, and according to some, seemed to approach a saturation value. It was also found that for a given impressed electromotive force the current depended very largely upon the temperature of the electrodes, particularly that of the cathode, and was practically inde-

[1] A preliminary account of some of the work described in the present paper was given in the Physical Review, Vol. XX., p. 186.

[2] Phys. Zeitschr., Band 5, Heft 3, pp. 76–81.

[3] Wied. Ann., XLII., 1891.

[4] Phil. Trans. A., Vol. CXCII., 1899.

pendent of the distance apart of the electrodes. This led some investigators[1] to advance the hypothesis that the ionization to which the conductivity of the flame was due, took place almost entirely at the surface of the glowing electrodes, and that throughout the volume of the flame there was little or no ionization.[2]

It was pointed out by the writer in the paper above referred to, that the total resistance encountered in the flame (R) may be considered in three parts, the resistance in the neighborhood of the cathode (R_k), the resistance in the neighborhood of the anode (R_a), and the resistance of the remainder of the flame between the electrodes (R_f) giving the equation $R = R_k + R_a + R_f$, and that if R_k or R_a were large in comparison with R_f, a variation in the distance apart of the electrodes would not change appreciably the value of R. Furthermore, it was shown that since R_k and R_a are functions of the conditions at the electrodes and of the current flowing between them, the above mentioned relations between current, electromotive force, and temperature of the electrodes, could be explained without denying the existence of a very considerable volume ionization throughout the flame.

The device employed by the writer for studying the electrical conductivity of flame gases and vapors has for its objects:

I. The reduction of the electrode resistances R_k and R_a to an order of magnitude equal to or smaller than that of the flame resistance R_f.

II. The maintenance of uniform conditions around the electrodes while the conditions throughout the conducting flame are being varied, as for example, by the introduction of the vapors of various salts.

III. The entire elimination of the electrode resistances, by determining the resistance, or conductivity, of a given section of the connecting flame from measurements of the current through that section and of the potential difference between the two faces of the section.

[1] H. A. Wilson, *ibid.*; J. J. Thomson, Conduction of Electricity through Gases, London, 1903, pp. 172 and 199.

[2] This view has been abandoned by H. A. Wilson in a recent paper, Phil. Mag., Vol. 10, No. 58, pp. 476–485, in which he takes the view of a volume ionization throughout the flame.

The first of these objects was accomplished by the employment of platinum electrodes (*P*, *P*, Fig. 1) coated with calcium oxide and heated in separate electrode flames. Such incandescent electrodes of calcium oxide have been shown by Whenelt[1] to possess the property of offering a very slight resistance to the passage of an electric current to or from a conducting gas. The resistance of the electrode flames was made very small by supplying the burners

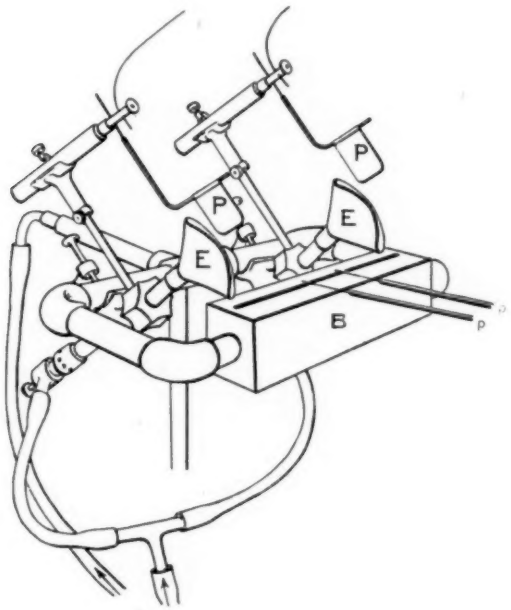

Fig. 1.

E, *E*, Fig. 1, with a mixture of gas and of air which had been blown through an atomizer containing a strong solution of potassium nitrate, the vapor of this salt being known to impart a very high degree of conductivity to the flame containing it. The flame under investigation was used as a connecting flame between the two electrode flames, and its resistance was made as great as possible by using, as a burner, a long narrow slot (0.1 cm. by 21 cm.) cut in a block of soapstone (*B*, Fig. 1). This burner gave a very broad, thin flame having a relatively large resistance.

[1] Ann. der Phys., Band 4, Heft 14, p. 425, 1904.

The second object was accomplished by having the supply of gas and air for the connecting burner independent of the supply for the electrode burners, so that the conditions in the connecting flame could be altered without in any way changing the conditions around the electrodes. The gas and air supplied to the connecting flame were both passed through suitable meters so that the volume of either consumed per minute could readily be measured. The type of meter used consisted of a small circular opening in a thin, metal diaphragm so mounted that the difference of pressure on the two sides of the diaphragm, when a current of gas or air was flowing through the opening, could be accurately measured by an inclined *U*-tube manometer containing xylene. A schematic diagram of one of these meters is shown in *M*, Fig. 8. Each meter was calibrated by connecting it in series with a standard gas meter, and the values of the manometer readings were determined in cubic feet per minute when gas or air was blown through. The conditions in the connecting flame could thus not only be varied independently of the electrode flames, but the volumes of gas, air, or spray supplied to the burner could readily be measured.

To accomplish the third object, the current through the flame was measured by connecting in series with the electrodes (*PP*, Fig. 1), a galvanometer of the d'Arsonval type, sensitive to about 10^{-8} amperes and provided with a universal shunt. The electromotive force employed was furnished by a battery of dry cells, and could be varied between about 1.5 and 200 volts. The difference of potential between the two faces of any section of the connecting flame was determined by inserting two fine, platinum wires (*pp*, Fig. 1) near the tip of the inner blue cone, and at a distance apart equal to the breadth of the section under investigation. The wires were connected respectively to the needle and to the middle point of the series of batteries used to impress a fixed difference of potential between the quadrants. Under these conditions the deflections of the electrometer needle were directly proportional to the difference of potential between the wires *pp* for all values of the potential to be measured.

The difference of potential between the wires *pp* was shown by the following experiments to be a true measure of the difference of

potential between the corresponding points in the flame. The introduction into, or withdrawal from the flame, of the electrometer wires, was found to produce no change in the current through the flame of as much as one per cent. of its value. The difference of potential across a breadth of 6 cm. of the connecting flame was measured by means of the electrometer wires in three steps of 2 cm. each, and again in a single step of 6 cm. the two measurements were found to agree within the errors of the readings. A further test of the correctness of the potential difference obtained by the use of the electrometer wires was made by measuring with them the potential difference across the connecting flame and also the difference of potential between either electrode plate and one of the electrometer wires inserted at the boundary between the electrode flame and the connecting flame. The sum of the three differences was found to be equal to the electromotive force impressed at the electrodes.

Measurements of the potential difference between the cathode plate and the flame around it under various conditions showed that this difference increased much more rapidly than the current between the electrodes, and it was found that by using a long connecting flame, a small impressed electromotive force (one or two volts) and a saturated solution of KNO_3 in the atomizer supplying the electrode flames the resistances at the electrodes could be made so small in comparison with the resistance of the connecting flame that they could be neglected without introducing any appreciable error. Under these conditions the conductivity of the connecting flame could be taken as directly proportional to the current for a given impressed electromotive force. In some cases it was found more convenient to determine relative conductivities in this way than by the use of the electrometer wires. A comparison of the two methods, however, showed that in all cases they gave the same results.

In this paper the term "conductivity of a given section of the connecting flame" will be used to designate the quotient obtained by dividing the current through the flame by the potential difference between the two faces of the section. Since the connecting flame was not rectangular in shape, but was more or less irregular

in its upper boundary, the lines of current flow and the equipotential lines in the connecting sheet of flame are not straight but are slightly curved, and therefore the "given section" above referred to is not a rectangular section. As, however, the measurements, were all relative, the shape of the section was unimportant so long as it remained the same. Furthermore, it was found that the size and shape of the upper portions of the flame had little or no influence on the total conductivity, as over 90 per cent. of the current was carried by the lower portions of the flame quite near the slot of the burner.

The experiments described in this paper have been made with flames consuming ordinary illuminating gas. The measurements are mostly relative, and the paper is more in the nature of a qualitative investigation into the source of ionization in flame gases and vapors than a quantitative study of the same. The writer hopes soon to be able to make a more quantitative study of the phenomena. The measurements already made have, however, led to a number of very important general relations which are given in the following sections.

I. A Saturation Current not Possible in the Combustion Cones of the Ordinary Bunsen Flame.

Some experiments were undertaken by the author in connection with Dr. J. Stark[1] for the purpose of ascertaining whether a saturation current could be obtained between two platinum wire electrodes, either clean or coated, with CaO placed very close together in the Bunsen flame. The results showed conclusively that no trace of a saturation current could be obtained under these conditions, but that for impressed electromotive forces of over 100 volts, the current increased more rapidly than the electromotive force. Under these conditions it was not possible to determine the relation between current and potential gradient in the flame, since the gradient could not be considered as uniform between the electrodes.

Later some experiments were undertaken by the author, in which the long connecting flame was used between the two electrode

[1] Phys. Zeitschr., Band 5, Heft 9, pp. 248–257.

flames. Various electromotive forces, up to 8,000 volts, were impressed at the electrodes, and the potential gradient and corresponding current in the connecting flame were measured as described in the introduction, the electrometer wires being placed in the inner blue cone of the flame and about 4 cm. apart. For

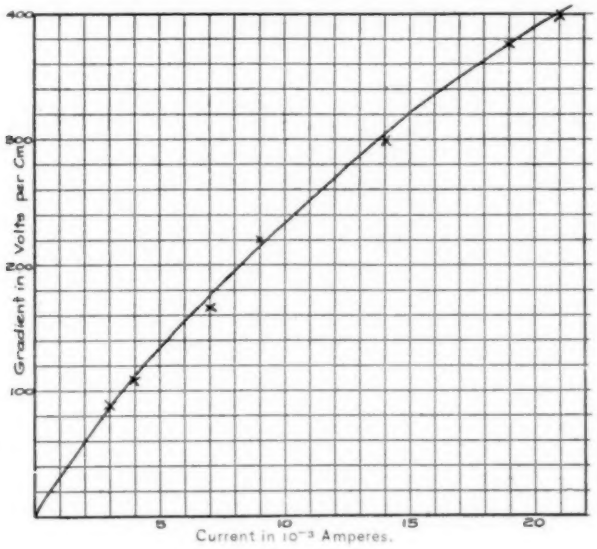

Fig. 2.

potential gradients ranging between 0.1 and 50 volts per cm., the current was found to increase directly as the potential gradient, the relation being a simple linear one. For gradients between 100 and 400 volts per cm., the current was found to increase more rapidly than the potential gradient. The results are shown in the curve, Fig. 2. When the impressed electromotive force was still farther increased, there were unmistakable evidences of ionization by impact, such as a sudden increase in the current, a decrease in the potential gradient and a marked increase in the temperature of the electrodes and of pieces of mica or platinum that might be placed in the connecting flame.

Experiments were also tried in which the electrode flames and the electrometer wires were placed in the outer blue cone of the connecting flame instead of in contact with the inner blue cone. The results, however, were similar to the above, showing that within

the combustion cones of the flame it is not possible to obtain a saturation current. Within these regions the rate of production of ions is so great that ionization by impact is produced before the potential gradient is great enough to remove the ions as fast as formed.

II. Electrical Conductivity of the Different Cones of the Bunsen Flame.

For the purpose of studying the electrical conductivity of the different parts of the Bunsen flame, a separable cone burner was constructed by placing over the slot in a soapstone burner similar to *B*, Fig. 1, a rectangular chimney of soapstone 1 cm. wide on the inside and 9 cm. high. Through small holes in the ends of the chimney, copper wires were inserted carrying thin platinum foil electrodes coated with CaO. The electrometer wires were inserted through small holes in one side of the chimney, about 4 cm. apart and directly between the electrodes. The holes were so spaced that the electrodes and the electrometer wires could be placed in either of the following positions: (1) In the inner blue cone, (2) in the space about a centimeter above the inner blue cone, (3) in the space just below the outer blue cone, (4) above the chimney in the outer blue cone.

In each of the above positions the electrometer wires were placed 4 cm. apart and directly between the electrodes, which were ordinarily kept about 8 cm. apart. The currents and the corresponding potential differences between the electrometer wires were measured in each of the above positions for a number of different impressed electromotive forces. The following are representative of the results obtained:

Position 1. — With a potential gradient of 12 volts per cm., the current was 2.7×10^{-4} amperes, and increasing the gradient increased the current in the same proportion.

Position 2. — A potential gradient of 9 volts per cm. gave a current of 4.5×10^{-7} amperes, and doubling the potential gradient increased the current to only 6.0×10^{-7} amperes.

Position 3. — A potential gradient of 10 volts per cm. gave a current of 3.5×10^{-8} amperes, and doubling the potential gradient did not appreciably increase the current.

Position 4. — A potential gradient of 9 volts per cm. gave a current of 2.1×10^{-6} amperes, and increasing the potential gradient increased the current proportionately.

On comparing the specific conductivities of the different parts of the flame from the above data, it should be kept in mind that the cross-sections of the blue cones carrying the currents in positions 1 and 4 were much smaller than the cross-sections of the intermediate gases carrying the currents in positions 2 and 3. The difference in specific conductivity between the blue cones and the intermediate gases is, therefore, even greater than would appear from the above data. From these data it appears that the specific conductivity of the gases in the inner blue cone of the Bunsen flame is about 1,000 times greater than the specific conductivity of the gases in the region just above the blue cone, and about 10,000 times greater than the specific conductivity of the same gases after ascending some 7 or 8 cm. above the lower cone. The measurements also show the specific conductivity of the inner cone to be about 100 times that of the outer cone.

While the measurements in the combustion cones showed no indication of a saturation current, the measurements made in the region between the two cones showed unmistakably the possibility of such in this region.

These measurements would seem to show that in the Bunsen flame, the source of the ionization is the chemical process of combustion taking place in the two cones of the flame, and that between and outside of these cones we have recombinations of the ions produced in the cones. Therefore the number of free ions per c.c. in the ascending gas diminishes rapidly as the gas is carried away from the regions of combustion.

In the case of the ordinary luminous gas flame where no air is mixed with the gas before it reaches the burner, it was found that the conductivity of the upper luminous portion of the flame was very small in comparison with the conductivity of the colorless, or faintly blue, lower portion. This was shown by introducing a sheet of mica across the flame so as to cut in two the upper luminous portion, when it was found that the current was not appreciably diminished. If, however, the mica were lowered so as to cut into

the lower non-luminous portion, the current was decreased and became zero when the mica sheet touched the burner. This shows that the chemical reactions taking place in the lower non-luminous portions of the ordinary gas flame are the ones chiefly productive of ionization, and that the consumption of the carbon particles in the upper luminous portions of the flame is accompanied by a relatively small amount of ionization.

III. Relation Between the Character of Combustion in a Gas Flame and its Electrical Conductivity.

The next experiments were for the purpose of comparing the electrical conductivities of flames consuming the same quantity of illuminating gas per minute, but having mixed with the gas various quantities of air or carbon-dioxide, so as to change the character and appearance of the flame. The burner used was the long, slot burner *B*, Fig. 1. Measurements of the conductivity of the ordinary, luminous type of gas flame and of the Bunsen type of flame consuming the same volume of gas per minute showed that the Bunsen flame possessed from one and a half to two times the conductivity of the luminous flame. When the volume of gas supplied to the burner was kept constant, and gradually increasing amounts of air mixed with it before feeding it to the burner, the character of the flame changed gradually from the luminous to the Bunsen type. In this transition five rather distinct types of flame could be recognized by the eye. The diagrams in Fig. 3 show roughly the

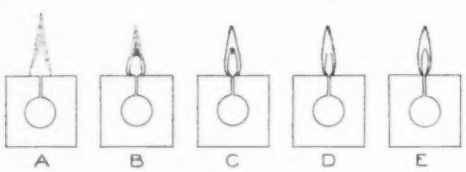

Fig. 3.

appearance of cross-sections of the different types. The ordinany, luminous type of flame is shown in *A*, no air being mixed with the gas before it was fed to the burner. The addition of air caused the flame to become shorter and change gradually to the type represented in *B*, which showed some rudiments of an inner blue cone,

and that portion of the carbon luminosity immediately above the inner cone seemed to be more luminous and of a less reddish hue than the rest. When the volume of air added was about equal to the volume of gas, the carbon luminosity had disappeared, with the exception of a faintly luminous cap to the rather feeble inner blue cone, type *C*. The further addition of air destroyed this luminous cap, and when the volume of air was something over twice the volume of gas, a cross-section of the flame had much the appearance shown in *D*. The inner blue cone seemed to have no well developed cap. The further addition of air caused the flame to assume the Bunsen type, *E*, and on continuing to increase the supply of air, the only effect was to cause the combustion cones to contract around the mouth of the burner.

Measurements were made of the conductivity of a given section of the above flame as gradually increasing amounts of air were added to a constant supply of gas of 0.18 cu. ft. per minute. The relation between conductivity and rate of supply of air is given

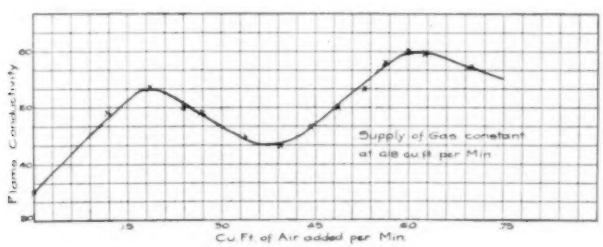

Fig. 4. Supply of Gas Constant at 0.18 cu. ft. per minute.

in the curve, Fig. 4. The measurements showed that the change in the character of the flame from type *A* to type *C* was accompanied by an increase in its conductivity, while the change from type *C* to *D* caused a decrease in conductivity. After the full development of the inner blue cone, the further addition of air caused the conductivity to increase to a maximum and then to decrease again, but rather slowly, as the velocity of efflux of the gases from the burner becomes greater and the combustion cones smaller.

A close relation between the character of the combustion taking place in a flame and its electrical conductivity was to be expected after the experiments described in section II., which showed that the

process of ionization was practically confined to the combustion regions of the flame, and was dependent on the type of combustion taking place in those regions. The number of free ions per cubic centimeter in any combustion region depends, however, in all probability, not only on the character of the chemical reactions taking place in that region, but also on the temperature and possibly the dilution of the gas in the region of combustion. Some such assumption would seem to be demanded for the explanation of the following phenomena:

When gradually increasing amounts of CO_2 instead of air were mixed with a fixed volume of the illuminating gas before delivery to the burner, the effect was to decrease the carbon luminosity and give a flame consisting of a single, thin, blue combustion sheet on either side of the burner slot. Measurements on the conductivity of the flame showed, however, no marked variation in conductivity until enough CO_2 had been added to destroy all the carbon luminosity, when the further addition of CO_2 caused a gradual decrease in the conductivity. The decrease was approximately proportional to the increase in the rate of supply of CO_2.

IV. Relation of Flame Conductivity to Rate of Consumption of Gas.

Measurements were next made for the purpose of determining the relation between the conductivity of a given section of the connecting flame and the rate of consumption of gas by the flame. For flames of ordinary illuminating gas unmixed with air (type *A*, Fig. 2), and consuming over a few hundredths of a cu. ft. of gas per minute, the relation between conductivity and rate of consumption of gas was found to be a linear one, although, for rates of consumption of over 0.15 cu. ft. per minute, with the burner used, the flame became very smoky. A typical set of readings is given in Fig. 5.

The conductivity of a shorter section of the connecting flame was measured for rates of gas consumption ranging from 0.01 cu. ft. to 0.16 cu. ft. per minute. For rates of consumption less than a few hundredths of a cu. ft. per minute, with the burner used, the flame consisted of a single blue cone with no carbon luminosity.

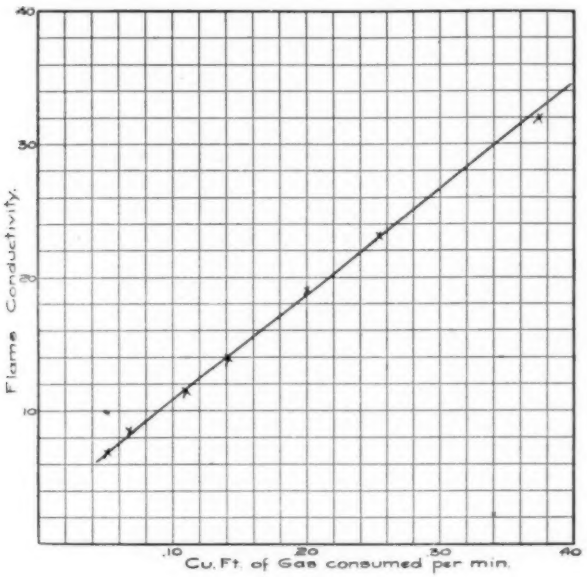

Fig. 5.

The character of the flame changed to the ordinary luminous type as the rate of supply of gas was increased. The relation between

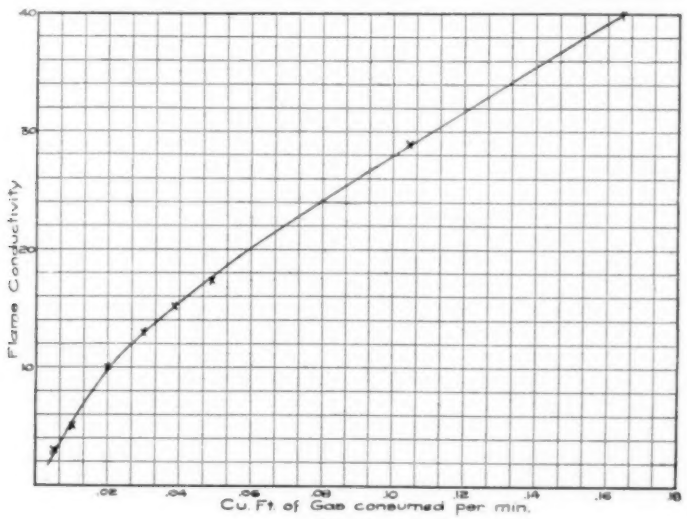

Fig. 6.

the rate of consumption of gas and the electrical conductivity of the flame is shown by the curve in Fig. 6. It was found that at first,

for the non-luminous flame, the conductivity increased quite rapidly with the rate of supply of gas. As the carbon luminosity became more pronounced the conductivity increased less rapidly, and finally, after the development of a flame of type *A*, Fig. 2, the relation between conductivity and rate of gas consumption became practically a linear one.

Other experiments were made in which air was mixed with the illuminating gas before feeding it to the burner, and as the supply of gas was increased, the supply of air was increased in the same proportion, so as to keep the ratio of air to gas a constant. This gave the same type of flame for all rates of supply of gas. Under these conditions measurements were made of the conductivity of the connecting flame for various rates of consumption of gas and for different ratios of gas to air. The result of a typical set of readings is

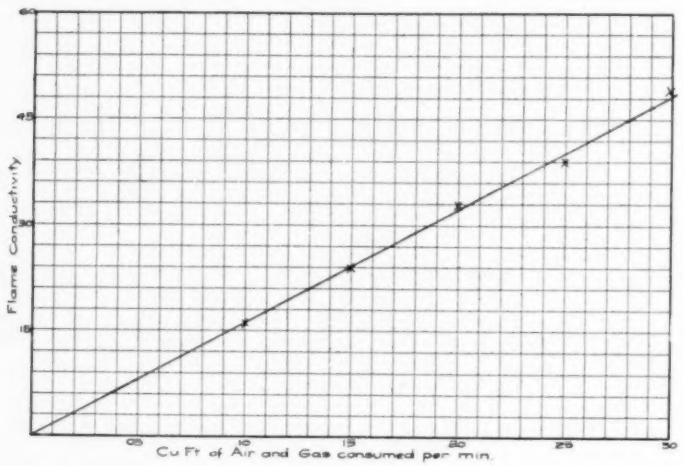

Fig. 7.

given in Fig. 7, the volume of air being equal to the volume of gas. So long as the character of the flame was kept the same and the ratio of gas to air remained constant, the electrical conductivity of the flame was found to increase directly with the rate of consumption of gas by the flame.

The above simple relation between the electrical conductivity and the rate of supply of gas to a flame is readily explained if we assume that for a given type of combustion the number of free ions per

cubic centimeter within the region of combustion remains constant. Increasing the rate of supply of gas to the burner would cause a proportional increase in the cross section of the combustion zone, and the electrical conductivity would increase directly as the area of this cross section.

V. Conductivity Imparted to a Flame by Salt Vapor.

Investigations on the conductivity imparted to a gas flame by the introduction of spray from a solution of salt were carried on by means of the apparatus shown in Fig. 8. The spray from the solu-

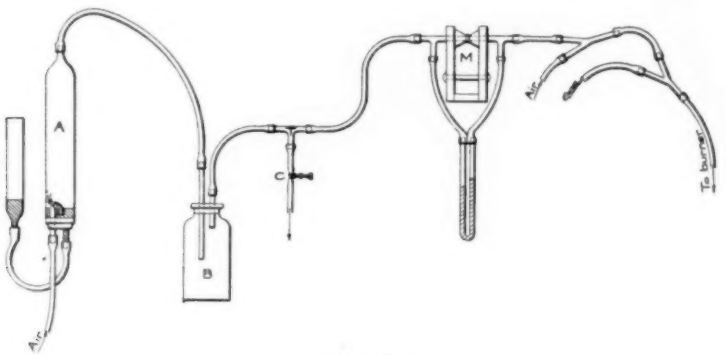

Fig. 8.

tion under investigation was obtained by passing a current of air or illuminating gas through an atomizer (*A*) containing the solution. The spray from the atomizer was led into a settling bottle (*B*) where the larger drops carried over from the atomizer were deposited. The spray was then conveyed through a T-tube to a meter (*M*) and thence to a Y-tube where it could be mixed with definite volumes of air or gas before being delivered to the burner. The diaphragm in *M* could readily be changed, and by means of the pinch-cock *C*, the flow of spray could be so regulated that for any size of opening in the diaphragm the difference in pressure on the two sides could be kept constant without changing the pressure on the atomizer. Under these conditions it was found that the flow through the diaphragm was directly proportional to the area of the opening. This device afforded two means of varying in a measurable manner the quantity of salt introduced into the flame : (1) Keep-

ing the opening in the diaphragm and the difference in pressure between the two sides the same, the concentration of the solution in the atomizer could be varied; (2) keeping the same solution in the atomizer, the size of the opening in the diaphragm in *M* could be altered and varying quantities of the spray admitted to the flame.

The conductivity imparted to the flame by the salt spray was determined by subtracting from the total conductivity determined in the usual way, the conductivity of the flame when consuming an equal amount of gas and of air which had been blown through the atomizer when it contained water in place of the salt solution. Whether the air was saturated with water vapor or dry seemed to make no difference in the conductivity of the flame.

Preliminary measurements showed that the conductivity imparted to the connecting flame by the introduction of salt spray varied greatly according to the character of the flame. Measurements of the relative conductivities imparted to a flame by different quantities of salt spray were also found to be quite different for the different types of flame. It therefore seemed desirable to investigate more carefully the effect that variations in the character of the flame would have on the salt conductivity imparted to the flame by a given amount of spray.

Experiments were undertaken for the purpose of determining the effect on the salt conductivity of gradually increasing the supply of gas to the burner while keeping the rate of supply of air and of salt spray constant. Increasing the supply of gas caused the flame to change gradually from a forced Bunsen flame of type *E* to a flame of type *B*, very rich in carbon luminosity. The rate of supply of air and spray from the atomizer through the meter (*M*, Fig. 8) was kept constant at 0.23 cu. ft. per minute. Measurements were made of the salt conductivity imparted to the flame by the spray from a solution of NaCl as increasing quantities of gas were mixed with the spray. The measurements were repeated when solutions of different concentrations were placed in the atomizer, the rate of supply of air and spray being kept constant at 0.23 cu. ft. per minute. The results are shown in the curves in Fig. 9. An examination of the curves shows that the salt conductivity increases at first very rapidly with the increase of gas. It reaches a maximum

when the rate of supply of gas is about equal to the rate of supply of air through the atomizer, giving a flame of type *C*. The salt conductivity then decreases, but very slowly, as the rate of supply

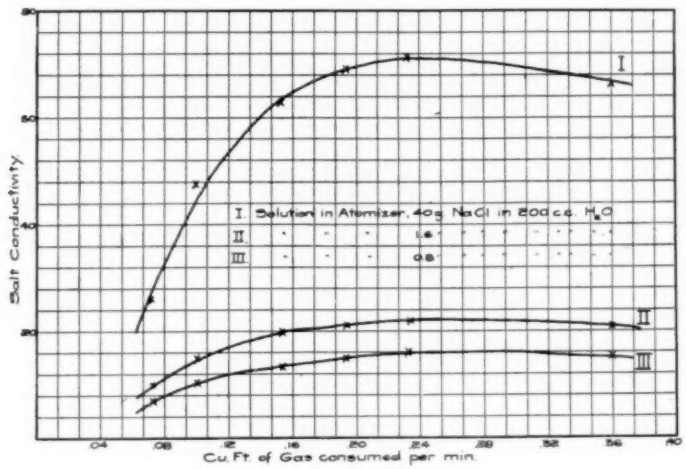

Fig. 9.

of gas is increased. A change in the concentration of the salt solution in the atomizer does not change the general character of the above relation.

Other experiments were tried in which the salt spray was introduced into the flame by blowing the gas itself through the atomizer. The supply of gas and spray from the atomizer was kept constant and gradually increasing amounts of gas supplied to the burner by a separate tube. Under these conditions the salt conductivity imparted to the flame remained almost constant, although the cross-section of the flame, due to the addition of the gas, was increased several times.

Other measurements of the salt conductivity imparted to the flame were made when the rate of supply of spray was kept constant and the rate of supply of gas and of air both increased in such a way as to keep the total volume of air equal to the volume of gas supplied. Under these conditions it was found that the salt conductivity increased directly with the rate of suppy of air and gas for all solutions of moderate concentration. When a very concentrated solution of NaCl was placed in the atomizer, the salt conductivity

imparted to the flame seemed to increase somewhat less rapidly than the rate of supply of air and gas. The results of measurements made with three different concentrations of salt solution in the

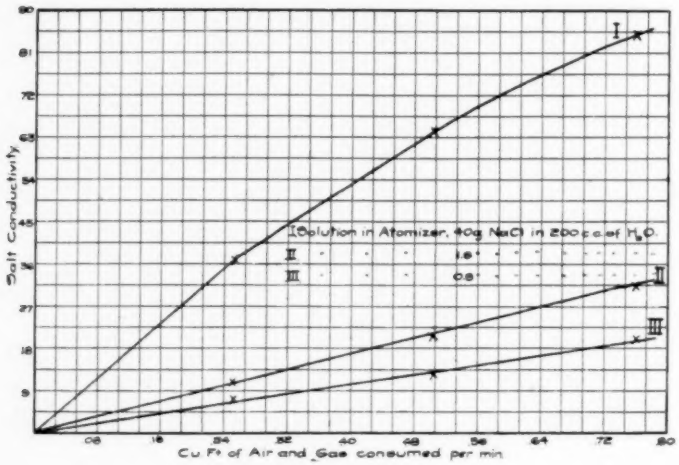

Fig. 10.

atomizer are given in the curves of Fig. 10, the volume of air was kept equal to the volume of gas supplied.

In the next experiments the illuminating gas itself was blown through the atomizer, and the rate of supply of gas and spray to the burner was kept constant at 0.17 cu. ft. per minute. The conductivity of the flame was then measured, as gradually increasing amounts of air were mixed with the gas and spray before delivery to the burner. Under these conditions the character of the flame changed from a flame of type *A* through the intermediate types to a forced Bunsen flame of type *E*. The measurements of the gas conductivity when pure water was placed in the atomizer are given

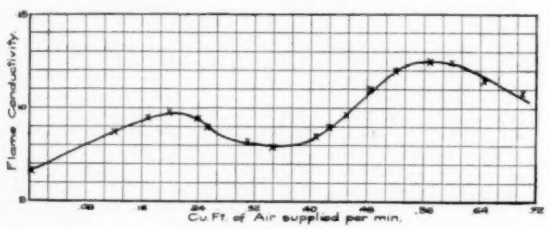

Fig. 11.

in the curve in Fig. 11. The measurements of the salt conductivity imparted to the same flame when solutions of NaCl of different concentrations were placed in the atomizer are given in the curves of Fig. 12. An examination of the figures shows that the mixture of

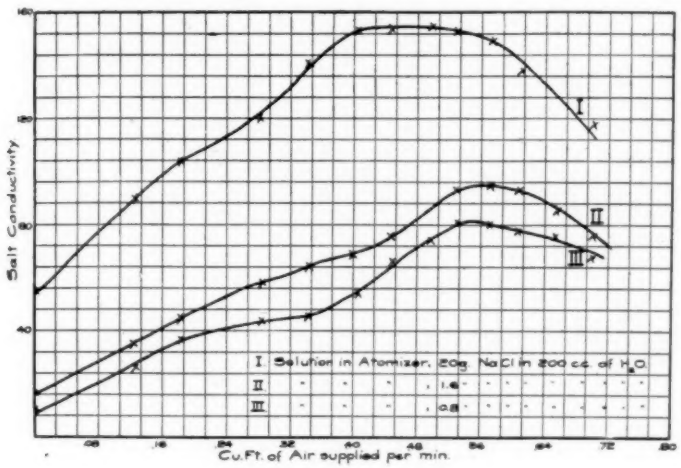

Fig. 12.

air and gas which gives the maximum conductivity to the pure flame gives also the maximum of salt conductivity. The addition of air to a flame of type *A* containing salt spray causes the salt conductivity to increase at first with the quantity of air added. This increase continues until the rate of supply of air is about equal to the rate of supply of gas, when the farther addition of air causes a less rapid increase in the salt conductivity until enough air has been added to give a flame of type *E*. Continuing the addition of air causes a more rapid increase in the salt conductivity which finally reaches a maximum when the volume of air is between three and four times the volume of gas. The ratio between this maximum of salt conductivity and the conductivity imparted by the same quantity of salt to the flame of type *A* when no air was mixed with the gas, was found to be quite different when different concentrations of the salt solution were used in the atomizer. The following are the ratios obtained :

Number of Grams of NaCl Dissolved in 200 cc. of H_2O.	Ratio of Maximum Salt Conductivity Imparted to a Flame of Type *E* to the Conductivity Imparted to a Flame of Type *A* Consuming the Same Quantity of Gas.
20	2.9
1.6	5.7
.8	6.8

These numbers show that the variation in the salt conductivity due to a variation in the character of the flame, on the addition of air, is much greater when the quantity of salt in the flame is small than when it is large. The increased quantity of salt ions in the flame seems to diminish in some way the effects of the changes tending to bring about an increase in ionization.

Experiments were also made in which gradually increasing amounts of pure oxygen instead of air were added to a fixed rate of supply of gas and spray. The results were of a similar character to those obtained by the use of air.

Another set of measurements was made in which gradually increasing amounts of CO_2 in place of air were added to the fixed rate of supply of gas and spray from the atomizer. For very dilute solutions of NaCl in the atomizer, the addition of CO_2 caused no change in the salt conductivity imparted to the flame until enough CO_2 had been added to destroy the carbon luminosity, when the farther addition of CO_2 caused a decrease in the conductivity. For the more concentrated solutions in the atomizer the salt conductivity seemed to decrease with the first addition of CO_2. The results of measurements made with three different concentrations of salt solution are given in the curves of Fig. 13. The rate of supply of gas and spray was kept constant at about 0.17 cu. ft. per minute.

Experiments were made with the separable cone burner described in Section II., when a large quantity of spray from a saturated solution of NaCl was mixed with the air and gas before delivery to the burner. Measurements of the current and potential gradient were made in the positions 1, 2, and 4 (see Section II.), with the following results:

Position 1. — With a potential gradient of 7 volts per cm. the current was 7.5×10^{-4} amperes.

Position 2. — A potential gradient of 0.7 volt per cm. gave a current of 7.5×10^{-6} amperes.

Position 4. — A potential gradient of 10 volts per cm. gave a current of 75×10^{-6} amperes.

In all these positions an increase in the potential gradient was accompanied by a proportional increase in the current. If, from the

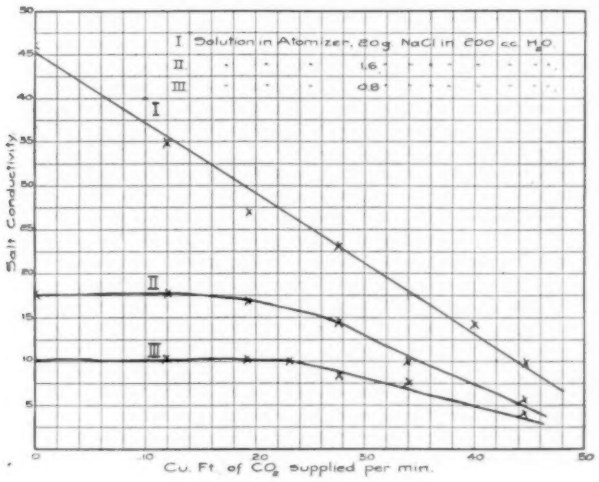

Fig. 13.

total conductivity of the different cones given above, we subtract the conductivity due to the flame gases given in Section II., we shall have numbers expressing, approximately, the salt conductivity imparted to the different cones of the flame. In this way it was found that the conductivity imparted to the inner blue cone by the salt spray was about ten times the conductivity imparted by the spray to the region just above the inner cone, and about two hundred times the conductivity imparted to the outer blue cone. The difference between the salt conductivity of the inner blue cone and the conductivity in the region between the two cones is seen to be very much less than for the flame gases themselves. (See results given in Section II.)

It seems difficult, if not impossible, to account for the phenomena described in this section on the assumption that the ionization of the salt spray in the flame is due simply to the high temperature of the flame. The temperature at a given point in the region of combustion in a flame of type *A* can certainly not decrease with the increase in the supply of gas to the flame. There would there-

fore be no good reason for assuming that the rate of production of salt ions per cu. cm. in this region of combustion would be diminished by increasing the supply of gas if the ionization were due simply to the temperature. Increasing the supply of gas would however, increase the cross-section of the combustion zone, so that one would naturally expect an increase in the total salt conductivity imparted to a flame of type A on the addition of gas. The experiments showed that the salt conductivity remained practically a constant for widely varying rates of supply of gas. When, however, a flame of type C was obtained by mixing air with the gas, the salt conductivity did increase in almost direct proportion to the amounts of gas and air added (see Fig. 10). Furthermore, the addition of air to a flame of type A, the rate of supply of spray and gas being kept constant, was shown to cause an increase in the salt conductivity (see first parts of curves in Fig. 12).

The above seems to warrant the conclusion that in order to have the salt spray ionized in the flame one must have not only the high temperature of the flame, but also the mixture of the spray with oxygen. Other conditions remaining the same, the salt conductivity imparted to a flame by the introduction of salt spray can be increased by the addition of air or oxygen.[1]

VI. Relation Between Salt Conductivity and the Rate of Supply of Salt to the Flame.

Experiments were next undertaken for the purpose of determining the effect on the salt conductivity of increasing the rate of supply of spray to a flame of type B consuming gas at a fixed rate. Three methods were tried for varying the rate of supply of spray.

1. The diaphragm in the meter M, Fig. 8, was changed and the pinch-cock C so adjusted that for different openings in the diaphragm the difference in pressure on the two sides remained constant. Under these conditions the rate of supply of spray to the burner could be increased by increasing the rate of supply of air in the same proportion. The constant rate of supply of gas to the burner was large enough to give a flame of type B for even the largest amount of air and spray. Under these conditions it was

[1] Some further results are given in the PHYSICAL REVIEW, Vol. XXII., page 113. On page 114, the 16th line from the top, instead of $Na = 6$, it should read $Na = 3$.

found that with rather concentrated solutions of NaCl in the atomizer, the salt conductivity imparted to the flame increased directly with the volume of spray supplied to the flame. With very dilute solutions, however, the salt conductivity seemed to increase a little more rapidly than the rate of supply of air and spray. The

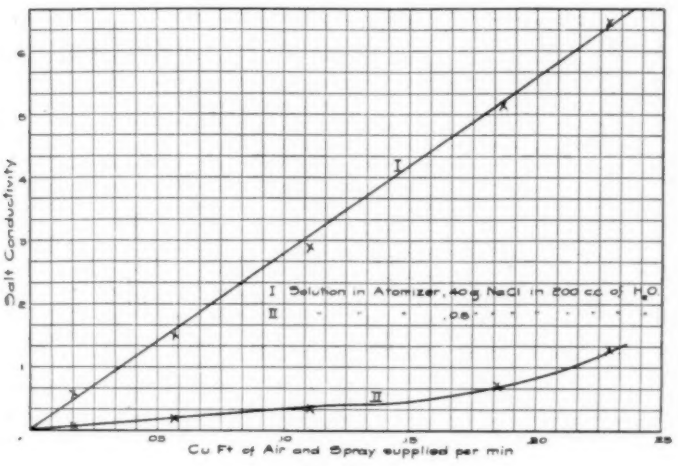

Fig. 14.

results of measurements made with two solutions of very different concentrations are given in the curves of Fig. 14.

2. In the above method of varying the supply of spray to the flame, the proportion of air to gas was also varied. To avoid this, a second method of varying the rate of supply of spray was tried in which, by means of an independent supply of air, the quantity of spray delivered to the flame could be varied without changing the proportion of air to gas.

3. A second method of accomplishing the same result would be to vary the concentration of the salt solution in the atomizer, keeping other conditions the same. Both of these methods were tried, and the results are given in the following table. The flame in both cases was of the type *B* having the volume of air less than the volume of gas.

The numbers in the first vertical column of the table are proportional to the salt conductivities imparted to the flame by the spray from a very concentrated solution of NaCl (40 g. in 200 c.c.),

when the area of the opening in the diaphragm was respectively 1, $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$ and $\frac{1}{24}$ of the area of the largest opening used. The numbers in the other vertical columns are proportional to the salt conductivities when solutions of $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$ and $\frac{1}{24}$ of the concentration of the above were used in the atomizer. The numbers in the horizontal rows of the table, therefore, are proportional to the salt conductivities imparted to the flame by spray from the different solutions when the area of the opening in the diaphragm remained the same.

Concentration of Salt Solution.

Area of Diaphragm Opening.	1	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{24}$	Ratio of Maximum to Minimum Salt Conductivity Due to a Variation in the Concentration of the Solution.
1	94	77	60	43	25	3.8
$\frac{1}{2}$	73	55	41	28	16	4.6
$\frac{1}{4}$	53	41	29	20	11	4.8
$\frac{1}{8}$	34	26	18	12	6	5.7
$\frac{1}{24}$	16	12	9	6	2.5	6.4
Ratio of Maximum to Minimum Salt Conductivity Due to a Variation in the Diaphragm Opening.	5.9	6.4	6.7	7.2	10.0	

The numbers representing the conductivities imparted to the flame by small quantities of the salt vapor are liable to a larger percentage of error than the numbers representing the larger conductivities. They were obtained, like the other numbers, by subtracting from the total flame conductivity the conductivity of the flame when water was placed in the atomizer instead of the salt solution. For small quantities of salt in the flame, however, the total conductivity was of the same order of magnitude as the conductivity of the flame with water in the atomizer, and since it was found difficult to maintain absolutely uniform conditions in the flame, these

small differences are liable to a possible error of as much as 25 per cent. for the very smallest conductivities.

In the vertical column to the right of the table are given the ratios between the salt conductivities imparted to the flame by a given volume of spray from the concentrated and from the most dilute solution. In the row of figures below the table are given the ratios between the salt conductivities imparted to the flame by the largest and the smallest volumes of spray from the solutions of different concentrations. An inspection of these ratios shows that as the total quantity of salt in the flame is decreased, the same percentage variation of the quantity causes a much larger percentage variation in the salt conductivity imparted to the flame. In other words, increasing the quantity of salt in the flame seems to retard the process of ionization.

A further inspection of the ratios shows that for certain rates of supply of the salt spray to the flame, the conductivity varies approximately as the square root of the rate of supply, but that for larger rates the variation is less rapid than the square root law would give, and for smaller rates it is more rapid. A number of measurements were made of the salt conductivity imparted to a flame of type *B* when a very dilute salt solution was used in the atomizer — about $\frac{1}{700}$ concentrated. They showed that under these conditions the conductivity was almost directly proportional to the rate of supply of the spray.

The experiments of this section give additional evidence in favor of the conclusion arrived at in the last section. The linear relation between salt conductivity and rate of supply of salt spray when the rate of supply of air was increased proportionately (see Fig. 14) shows that the presence of oxygen plays as important a rôle in the phenomena of ionization of the salt spray as the high temperature of the flame.

When the rate of supply of gas and air was kept constant and the rate of supply of salt spray was increased, the experiments showed that for extremely small rates of supply of the spray, the salt conductivity increased in almost direct proportion to the rate of supply of the spray. As the quantity of the salt in the flame became larger, however, the conductivity was found to increase much

less rapidly than the rate of supply of salt. This would seem to be due to a decrease in the proportion of oxygen to salt spray, owing to which, a smaller proportion of the spray is ionized.

VII. Relation between Luminosity and Conductivity Imparted to a Flame by the Vapor of a Salt.

In a previous paper[1] the writer described some experiments on the relation between the luminosity and the conductivity imparted to a flame of the Bunsen type by the vapor of NaCl or of LiCl, when the luminosity was varied by the introduction of the vapor of chloroform, and it was shown that the relation was practically a direct one, the vapor of the chloroform reducing the conductivity in the same proportion as it reduced the luminosity.

The relation between luminosity and conductivity has also been determined when the luminosity was varied by varying the amount of spray introduced into the flame, either by changing the concentration of the solution in the atomizer or by changing the size of the opening in the diaphragm in *M*, Fig. 8. The sodium luminosity of a section of a low thin flame of the Bunsen type was determined by forming an image of the section on the slit of one of the spectroscopes of a Brace spectrophotometer, the filament of an incandescent lamp being used before the other slit for comparison. The conductivity of the same section of the flame was determined in the usual way by inserting the electrometer wires about 1 cm. apart and one on either side of the section. A number of simultaneous measurements of the conductivity and luminosity imparted to the flame by the vapors of either sodium or lithium chloride showed that varying the quantity of vapor in the flame by changing either the concentration of the solution in the atomizer or the size of the opening in the diaphragm in *M*, Fig. 8, or both, caused the luminosity to vary in the same proportion as the conductivity. In all these measurements the salt conductivity and luminosity were determined by subtracting from the total, the conductivity or luminosity due to the flame when water was placed in the atomizer. The measurements shown in Fig. 15, for NaCl, are representative of the results obtained.

[1] Phys. Zeitschr., Band 5, Heft 6, pp. 157–159.

A number of other measurements were made when a sheet of mica, which was found to be quite free from sodium, was inserted

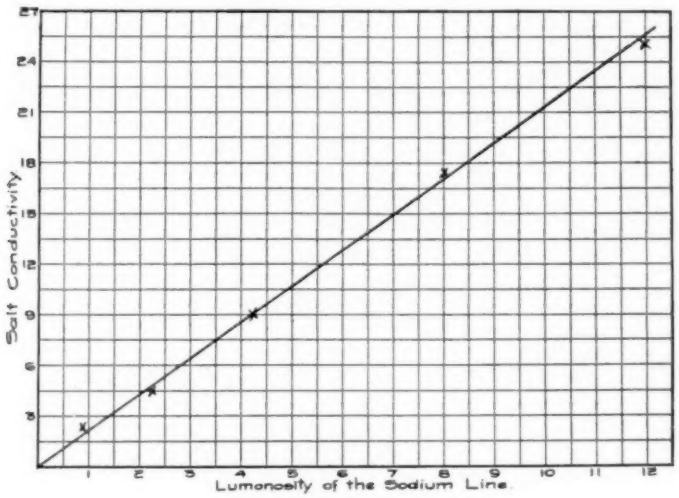

Fig. 15.

across the flame so that the lower edge of the mica was about 1 cm. above the burner. The electrometer wires were placed about half

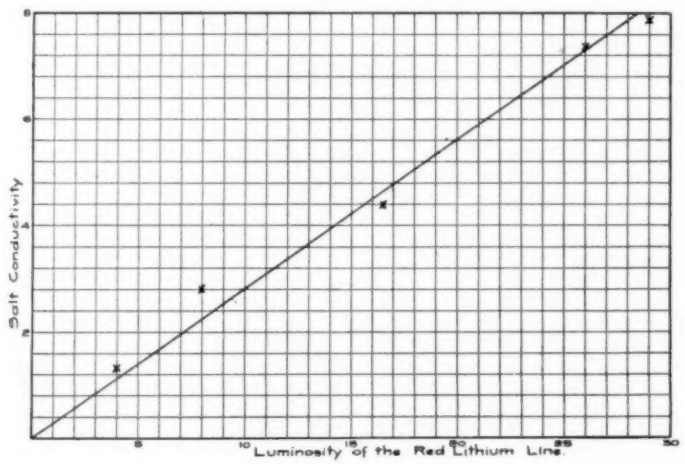

Fig. 16.

a centimeter apart, one on either side of the mica, and just above the burner. An image of the section of the flame between the lower

edge of the mica and the burner was formed on the slit of the spectroscope. Simultaneous measurements of the luminosity and conductivity imparted by the salt vapor to this section were made when the character of the flame was varied by varying the supply of air and gas, and keeping the rate of supply of spray to the flame constant. The relation between luminosity and conductivity, under these conditions, was also found to be a simple, linear one. A representative set of measurements for LiCl is given in Fig. 16. The conductivity measurements for the lithium salts are liable to a larger percentage error than those for sodium, owing to the smaller conductivity imparted by lithium salts to the flame.

The foregoing results show that when the luminosity imparted to a gas flame by the vapor of either sodium or lithium chloride is varied by varying the rate of supply of salt or by varying the character of the flame, the electrical conductivity imparted to the flame by the salt vapor is varied in the same proportion.

The relation between the electrical conductivity and the luminosity imparted to a flame by the spray from a solution of $CaCl_2$ did not seem to be so simple a one as for the salts of lithium and sodium. Owing to the relatively small conductivity imparted to the flame by the salts of calcium the measurements are liable to a larger percentage error and no very satisfactory results have as yet been obtained.

PHŒNIX PHYSICAL LABORATORY,
COLUMBIA UNIVERSITY.

CONDUCTIVITY OF VAPOR FROM THE MERCURY ARC.

By C. D. Child.

THE ease with which an electric current passes through the vapor of a mercury arc is well known. The experiments here described show that the vapor in the neighborhood of the arc also has a high conductivity and that the cause of the ionization there found is perhaps different from the causes of ionization which have heretofore been studied. The experiments were commenced for the purpose of finding the velocity of the ions in the mercury arc by the method which had been used in studying their velocity when drawn from a flame,[1] but it was found that in the case examined new ions are produced in all regions in the neighborhood of the arc, so that the method is not applicable. The investigation was, therefore, turned to a study of these ions.

Apparatus. — The apparatus used is shown in Fig. 1. *A* and *B* are two bulbs containing the mercury, the arc being formed by the common method of tipping the tube. *C* is a platinum wire used to draw the ions from the arc, *D* is one to determine the potential near to *C*, and *E*, to determine the potential of the arc.

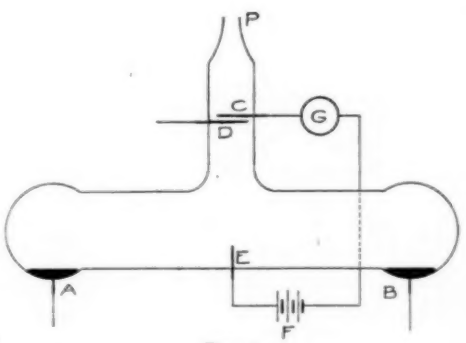

Fig. 1.

The potential difference between *C* and *E* was produced by the battery *F* and the current between these points was measured by the galvanometer *G*. *P* is the connection to the pump.

[1] Phys. Rev., 12, 65.

There is an objection to this arrangement in that E does not have the same potential as the arc about it, except when no current is flowing from E. A different arrangement was tried by putting a shunt between A and B and placing the battery and galvanometer between C and the middle of this shunt. But it was found that the middle of the arc did not have the same potential as the middle of the shunt. This was shown by placing an electrometer between the two points. Moreover the potential of E was continually varying. Whenever the mercury in A or B moved or even when the end of the arc shifted over the mercury, the potential of E changed. As a result the arrangement shown in the figure was used. This at least, gave results somewhat consistent with themselves and its disadvantages did not interfere with showing the principal facts for which this form of the apparatus was used.

The length of the tube was 13 cm. and the inside diameter 2.1 cm. The platinum wires were .45 mm. in diameter. The branch tube was 1.4 cm. in diameter. The distance of C from the middle of the tube AB was 6 cm.

Current between C and E Dependent upon Time. — On examining the current between C and E, it was found that when the arc was first started, the current was small, that it rapidly increased, and then decreased. This increase varied much at different times, but as an example a set of readings taken when the potential difference between C and E was 13 volts is given in Table I. The current through the arc was 4.5 amperes, and the pressure of the gas .2 mm. The first column gives the length of time that the arc had been running; column 2, the current when C was positive; and column 3, when it was negative.

TABLE I.

Time in Sec.	Current when C was Positive.	Current when C was Negative.
5	28×10^{-4}	5.7×10^{-4}
10	55	2.8
20	130	1.7
30	110	1.2
60	51	.57

The change in the current was not caused by the charge on C, for the conductivity was found to vary the same whether C was charged positively or negatively or was uncharged. It was found that the current became large much sooner, if the tube was hot when the arc was started, also that a glow gradually crept up the tube from the arc, and the conductivity became much greater when the glow reached C. The front of this appeared to be the boundary region between the hot mercury vapor and the residual gases which it was pushing out, for in this region the drops of mercury first began to appear on the sides of the glass.

Effect of Changing the Potential Difference. — Next the potential difference between C and D was varied, keeping the other conditions the same as before. With each potential difference the largest current which was observed at any time is given. Column 1 gives the potential difference; column 2, the current when C was positive; column 3, that when it was negative.

TABLE II.

Potential Difference between C and E.	Current with C Positive.	Current with C Negative.
1.5		5.1×10^{-4}
2.5		5.1
5	20×10^{-4}	5.4
8	68	5.4
11	100	5.4
13	128	5.4

With the first two voltages given with C connected to the positive side of the battery the current flowed against the E.M.F. of the cells, showing that there was an E.M.F. between C and E greater than 2.5 volts. E.M.F.'s of more than 13 volts were not used, because with so large currents the potential difference between E and the arc must become appreciable.

When the battery was placed between C and the middle of a shunt about AB, the results were much the same, except that with potential differences about 12 or 13 volts and with C positive, an arc was liable to form having C for the positive end.

The Internal E.M.F. between C and E. — The internal E.M.F.

between C and D was examined by balancing it against a variable potential difference. C was found to be negative at first, becoming positive, however, before the maximum conductivity of the gas occurred, and remaining positive.

A set of data taken are given in Table III. Column 1 gives the time in seconds from the starting of the arc and column 2, the E.M.F. in volts. The minus sign indicates that C was negative with respect to E. After the first four observations C was positive.

TABLE III.

Time in Sec.	E.M.F. in Volts.	Time in Sec.	E.M.F. in Volts.
9	−2	99	3.3
16	−3	106	3.5
33	−1.5	112	3.6
40	−1	121	3.8
44	+ .5	133	4
52	2.3	144	4.3
67	2.6	163	4.5
75	2.7	178	4.6
89	3	209	4.4

Several sets of observations were taken all similar to this. In general the change from negative to positive occurred sooner than in the data given above. It occurred at approximately the same time as that at which of maximum conductivity occurred.

The Potential Difference between C and D. — The potential difference between C and D when a current was flowing between C and E was examined by a quadrant electrometer. It was found that when the arc was first started the potential difference between C and D was nearly as great as that between C and E. After a few seconds it gradually decreased until the former was about half of the latter. This shows even more conclusively that the gas itself, aside from the layer about the electrode C, has a very high conductivity.

The experiments thus far bring out clearly three facts; first, that the gas in the branch tube is highly conducting; second, that this conductivity is greatest when the luminous part of the vapor first reaches the electrode; and third, that there is an E.M.F. in the branch tube.

Ions do not Come from the Arc. — The next experiments were undertaken for the purpose of determining whether the current between C and E was carried by ions coming from the arc, or by ions produced in the neighborhood of C. The branch tube was replaced by one having four electrodes as shown in Fig. 2. CD and EF were connected to separate E.M.F.'s which could be varied at will. If the current was carried by ions coming from the arc, it was expected that they would all be drawn out of the vapor by CD leaving none for EF.

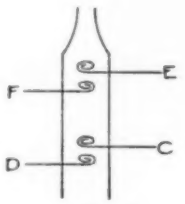

Fig. 2

In the experiment as tried the distance from C to the middle of the main tube was 5 cm.; from D, 5.5 cm.; from E, 8.3 cm.; and from F, 8.8 cm. The wires were platinum wires .45 mm. in diameter and coiled as in the diagram. The pressure of the gas remaining in the tube was .1 mm.

The current through CD was first examined and it was found that this current varied appreciably with the time and that it also depended on the direction of current between C and D. There is given in Table IV. the current at different times. Column 1 gives the number of seconds after the arc was started; column 2, the corresponding current in amperes, when C was positive; and column 3, that when it was negative. The E.M.F. in the circuit was 13 volts.

TABLE IV.

Time in Sec.	Current with C Positive.	Current with C Negative.	Time in Sec.	Current with C Positive.	Current with C Negative.
10	2.8×10^{-4}		85		17×10^{-4}
15		23×10^{-4}	90	5.1×10^{-4}	
20	14		95		10
25		45	100	2.8	
30	28		105		8.5
35		68	110	2.3	
40	40		115		5.7
45		85	120	1.7	
50	45		125		4.5
55		91	140	1.1	
60	34		145		3.4
65		63	160	1.1	
70	14		165		2.8
75		28	180	1.1	
80	8.5		185		2.3

It was noticed in making these observations that the time of maximum conductivity occurred a few seconds after the luminous part of the tube reached *CD*. Again the maximum current between *E* and *F* occurred shortly after the luminosity first reached that part of the tube.

The current through *CD* was then tested to learn whether it was "saturated." The data are given in Table V. Column 1 gives the potential difference between *C* and *D* in volts; column 2, the maximum current in amperes which flowed at any time with *C* positive; and column 3, that with *C* negative.

TABLE V.

Potential Difference.	Current with *C* Positive.	Current with *C* Negative.
1.2	24×10^{-4}	32×10^{-4}
2.5	42	62
5	42	83
9.5	49	97
13	57	110

The current between *C* and *D* would then appear to be "saturated" with only 5 volts, the increase after this, no doubt, being due to the fact that with stronger fields ions which are produced at greater distances from the electrodes are drawn up to them.

The current between *E* and *F* was found to vary in the same way, although it was at all times less than that between *C* and *D*, and the difference between the current flowing from *E* to *F* and that from *F* to *E* was not nearly as great as the difference in the two directions between *C* and *D*. The maximum current between *E* and *F* was 14×10^{-4} ampere.

The current through *EF* was further examined first when a current was flowing through *CD* and then with this current removed. The potential difference between *C* and *D* was 13 volts. This was more than enough to "saturate" the current, so that we had reason to believe that all of the ions passing between *C* and *D* were removed when this potential difference was applied. The current between *E* and *F* was, however, found to be the same whether any was flowing between *C* and *D* or not.

The current through *EF* was next tried together with a current through *CF*, *EF* being connected to an E.M.F. of 1 volt and *CF* to 13 volts, *F* being positive with respect to both *C* and *E*. In this case the current through *EF* was decreased from .95 to .85 milliampere, when the connection was made for the current to flow between *E* and *D*.

It would thus appear that none of the ions which carry the current between *E* and *F* come from the part *CD* and that but few of them are produced between *C* and *F*; that is, in general the ions found outside of the arc do not come from the arc, but are produced in the immediate neighborhood of the place where they are found.

Current not over Surface of Glass. — In all of these experiments there has been nothing to prove that the current did not flow over the surface of the glass. It is conceivable that the hot mercury vapor should make the surface a conductor. A coil of steel wire which pressed tightly against the surface of the glass, was, therefore, inserted between *C* and *D* as in Fig. 3. This was connected by a platinum wire to the outside at *E*. *C* was also extended so as to pass through the coil without touching it. *C* and *D* were then

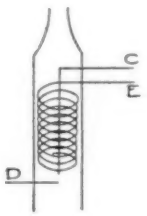

Fig. 3.

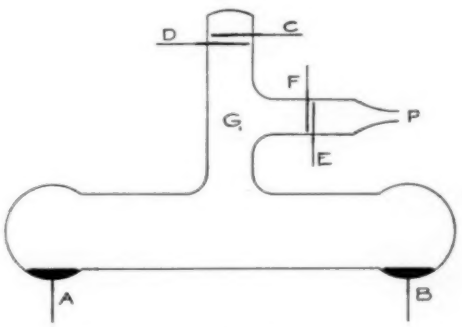

Fig. 4.

connected as before through a galvanometer and a cell, a storage cell of 2 volts was used in this case. It was found that the current between *C* and *D* was the same (approximately .002 ampere) whether *E* was kept at the potential of *C* or at that of *D*. This showed conclusively that the current passed through the gas and not over the surface of the glass.

Current not Caused by Rays from Arc. — It was thought that possibly rays were being given off from the arc that were making the space above it conducting. An experiment was, therefore, tried with a tube as in Fig. 4. The distances between *C* and *D* and between *E* and *F* were both approximately .5 cm. The distance from *D* to *G* was 3.5 cm. and that from *F* to *G* 4 cm. *P* was connected to the pump. Both *CD* and *EF* were connected to a galvanometer and a gravity cell.

It was found that an appreciable current first began to flow through *CD*, but that after 15 or 20 seconds the current between *E* and *F* became the larger. These experiments indicate that the ions are not produced by rays from the arc, otherwise the current between *C* and *D* in Fig. 4 would be the larger.

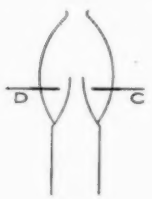

Fig. 5.

A tube was made as in Fig. 5, but with this there was no luminosity between *C* and *D*, nor was there any appreciable current between them at any time.

The experiments, therefore, show that the current does not flow over the surface of the glass, that it is not carried by ions from the arc, and is not produced by rays from the arc.

E.M.F. between C and D. — Examination was then made of the E.M.F. between *C* and *D*. It was measured by balancing it against a variable potential difference as when measuring E.M.F. between *C* and *E*. It was found that this E.M.F. behaved quite differently under different circumstances. When the electrodes were two coils of wire as in Fig. 2, the upper one was continually negative.

In one experiment it happened that the E.M.F. was observed when the upper electrode was a coil of platinum wire as before and the lower one a straight platinum wire as *C* in Fig. 1. With this arrangement the upper one was first positive and then negative, and finally positive again. This was found with three different tubes.

However in another tube with a similar coil above and a straight wire below and with other conditions the same, as far as was known, there was only one change of sign of the E.M.F., the coil being first positive and then negative. The data taken with this tube are given in Table 6, column 1 giving the time in seconds, and column 2, the E.M.F. in volts.

TABLE VI.

Time in Sec.	E.M.F. in Volts.	Time in Sec.	E.M.F. in Volts.
30	+.30	108	−.17
38	+.07	119	−.28
55	+.07	125	−.38
68	+.04	155	−.43
80	−.04	185	−.40
89	−.07	220	−.35
98	−.11		

It is not known why these different results were obtained. The pressure of the gas left in the tube was approximately .1 mm. in each case. There were some reasons for believing that the amount of water vapor left in the tube had some effect, but this has not yet been proven. The effect is no doubt due in some way to the greater mobility of the negative ions, but it is difficult to see just how this could produce the observed results. It needs, in fact, a much more careful study than I can at present give it, in order to give any satisfactory explanation.

Cause of the Ionization. — We see that the experiments have shown that the conductivity of the gas is produced neither by the ions from the arc, nor by rays from the arc. At first it was thought that the ions were produced by the high temperature, mercury vapor possibly ionizing more easily than other gases. The temperature, however, is not very high, and we have as yet no proof that even very high temperatures will produce ionization.

A different explanation has been suggested by Prof. Ernest Merritt, one which has much in its favor. According to this, when ions first recombine, their union is more or less incomplete. Each ion before recombining may have been a cluster of atoms with a positive or negative charge added. Two such oppositely charged clusters might become attached without the charges coming into the intimate relation which is needed for complete equilibrium. Some of these incomplete combinations might again break up much as the atoms of radium are supposed to do when subjected to some unusual atomic force. We might look upon such a group of atoms as radio-active matter produced artificially. Such a group would not be acted on by electrical forces, so that they would pass *CD* in

Fig. 3 and yet might be split up again into ions by the time they had reached *EF*.

It seems quite possible that such groups would be more apt to be formed with a mixture of gases at comparatively low temperature than with a single gas at high temperature. This would explain the fact that the conductivity of the gas is the greatest in the region where the mercury vapor is condensing. This is the boundary region consisting of the residual gases left in the tube and the mercury vapor which would be pushing them on. In the parts of the tube nearer the arc the continual flow of mercury vapor would have carried the other gases out and there would be nothing but mercury vapor and this would be at a high temperature. This is the region which we find has but small conductivity.

The E.M.F. Oscillatory. — When working with the arrangement shown in Fig. 3, it was noticed that the wire extending from *D* vibrated rapidly. It has already been found that the current through the mercury arc has rhythmic variations. A telephone was therefore connected directly between *C* and *D*. This gave a very distinct tone. The current through the arc was then passed through the primary of an induction coil and the secondary was connected to the telephone. This gave the same tone that had been produced when the telephone was connected between *C* and *D*. These experiments were tried with the current from a storage battery, in order that the fluctuations of the dynamo might be eliminated.

It was thought that possibly this rapid variation of the current through the arc might be aiding in the ionization of the gas, and an attempt was therefore made to get rid of these variations. The tube shown in Fig. 2 was used. Tin-foil was wrapped around the tube between *EF* and the main tube and *C* and *D* were connected to this foil, and this was then connected to the ground, but as far as could be detected this arrangement made no difference with the humming in the telephone. It certainly made no appreciable difference whether the tin-foil was connected to the ground, or left insulated. This experiment, therefore, showed nothing, except that it is very difficult to get rid of the effect due to the fluctuation of the current.

The effect could, however, be entirely stopped by connecting *C* and *D* by wire outside of the tube, showing that the humming was

produced by an E.M.F. within the tube and not by a magnetic induction outside of it.

Summary. — The following facts have been brought out by this investigation. The space in the tube connected with a mercury arc becomes highly conductive. A luminous space gradually spreads out from the arc and the front of this region has the greatest luminosity and the highest conductivity. This conductivity is not due to ions coming from the arc, nor to rays sent out by it. It is not due to any leakage over the surface of the glass. It is probably not due to the high temperature of the gas. A probable explanation is that when ions first recombine, they are in a condition of unstable equilibrium much like the atoms of radio-active matter, and often break up again, this being a form of ionization which has not heretofore been studied.

There is an E.M.F. between electrodes inserted in different parts of the tube. This is possibly due to the more rapid diffusion of the negative ions.

Aid was received from the Carnegie Institution in purchasing the apparatus used in this work, and I desire at this time to express my thanks to the Institution for the grant.

COLGATE UNIVERSITY, October, 1905.

THE ELECTRICAL PRODUCTION OF OZONE.

BY ARTHUR W. EWELL.

OZONE is produced by certain chemical reactions, by ultra violet light, by the electrolysis of certain solutions and (the most efficient method) by the extensive, continuous conduction of electricity through oxygen or air. Sparks produce little ozone and rapidly decompose any ozone already present. A gas exhibits this extensive conductivity (*i. e.*, is conducting throughout a large volume) if, either one of the electrodes, to which a high potential is applied, possesses sharp points or if an alternating current is employed and the electrodes are separated by the gas and a dielectric such as glass. Professor Warburg and the writer have quite exhaustively studied the production of ozone with the first type of ozonizer.[1] The maximum yield of ozone per coulomb was about 0.1 gr. With atmospheric air and the point electrode positive, the best yield in grams per kilowatt hour was about 27 and with an alternating current, or points negative, about 13. The temperature and pressure of the gas were found to be of small importance if the density remained unchanged, a result applicable to any method of ozonization.

A. W. Gray has studied one form of the second type of ozonizer, the dielectric being glass.[2] He found that the yield of ozone increased with the potential, and for the highest potential (12,240 volts for .062 cm. of oxygen and .168 cm. of glass) the yield was .225 gr. per coulomb. Neither the dielectric, nor the form of the electrodes nor their distance apart could be varied. No conclusive experiments were made with different gas velocities or ozone densities and the ozone density was very low.

Moreover a commercial alternating current was not employed. Dr. Gray used successive charges and discharges of a large con-

[1] Annalen der Physik, 17, 1905, p. 1.

[2] PHYS. REV., CIV., Nov., 1904, p. 347.

denser, periodically charged by an influence machine. The great discrepancy between the yields of ozone with the two types of ozonizer, and the enormous discrepancies in the claimed efficiency of the different commercial modifications of the two general types [1] led the writer to undertake a study of the production of ozone with other electrodes than the point and plate which had already been so carefully studied.

Apparatus. — The final form of apparatus will be described. It is diagrammatically sketched in Fig. 1. The air is dried by passing through calcium chloride and concentrated sulphuric acid. A tube containing glass wool caught any bubbles of acid. The air then

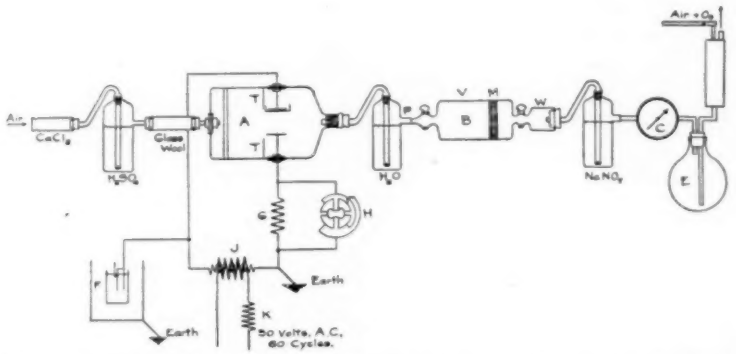

Fig. 1. Schematic Figure of Apparatus. *A*, ozonizer; *B*, sample tube; *C*, gasometer; *D*, Geryk pump; *E*, reservoir; *F*, repulsion voltmeter; *G*, non-inductive resistance; *H*, Dolezalek electrometer; *J*, transformer; *K*, rheostat.

entered the ozonizer. This was a four-liter bottle in which the electrodes (one form of which is illustrated) were mounted upon brass rods which passed through holes in the sides and were secured by nuts and asbestos washers. The bottom of the bottle had been carefully cracked off to give access to the interior, and when replaced and sealed with adhesive paper strip was secure and gas-tight. A brass tube with nuts and asbestos washers passed through the bottom and a glass tube passed through a rubber stopper in the neck. This stopper was protected from the ozone by paraffin and asbestos. Glass shields, *T*, *T*, confined the gas current to the space between the electrodes. Leakage over the glass surface was neg-

[1] For description of commercial ozonizers, etc., see article by the writer in Electric World for August 12, 1905.

ligible, for the current was infinitesimal until the potential was sufficient to make the air conducting and then rapidly increased with increasing E.M.F. (see Fig. 4).

The ozonized air bubbled through fresh distilled water to absorb any nitrous oxide[1] produced with the ozone and then traversed in succession the sampling tube, sodium nitrite, to absorb the ozone, a gasometer, a ten-liter reservoir and the (Geryk) pump.

The three bottles were gas-washing bottles, in the necks of which fitted, with ground glass joints, the tubes figured, the lower ends of which were closed except for a circle of small holes near the bottom. At the joint marked *P*, one glass tube loosely fitted over the other, the joint being made tight by a ring of fine bleached cotton.

The main part, *V*, of the final sample tube had a volume of 680 c.c. A rubber stopper made connection between the funnel-shaped part, *W* (capacity = 60 c.c.), and the figured glass tube. The tube could be taken apart for cleaning at the ground-glass joint *M*.

An alternating current of 60 cycles was employed throughout all the experiments. The transformer was one limb of one designed by Prof. H. B. Smith. Its capacity was 100 k.w. and at full capacity its secondary e.m.f. was 500,000 volts. One side was grounded and the potential of the other side was determined by a mirror repulsion voltmeter. The latter was calibrated by measuring with calibrated Kelvin and Braun electrostatic electrometers the voltage across successive groups of windings of the secondary on open circuit and summing up. A calibration curve is given in Fig. 2. The current was determined by measuring with an idiostatic Dolezalek electrometer the fall of potential across a non-inductive resistance. For calibration, known alternating currents of the same frequency were employed. The calibration changed somewhat. The curve for July 5 is given in Fig. 2.

An experiment was conducted as follows: When the current and potential were satisfactory the air current was maintained for at least five minutes at the desired speed, as indicated by the gasometer readings per minute. Then the nearer cock of the sample tube was closed and immediately after, the farther cock. The sample tube was then disconnected and 50 c.c. of a solution of potassium

[1] Warburg, Annalen der Physik, 17, 1905, pp. 22.

iodide (10 g. JK. in 500 c.c. H_2O) was poured into *W*. By opening the upper cock this was introduced into *V* and thoroughly shaken with the ozonized air. The amount of ozone could be roughly judged by the yellow color due to the liberated iodine. The solution was then drawn out, an equivalent amount of sulphuric acid added and adding starch, was titrated with a one-fiftieth normal

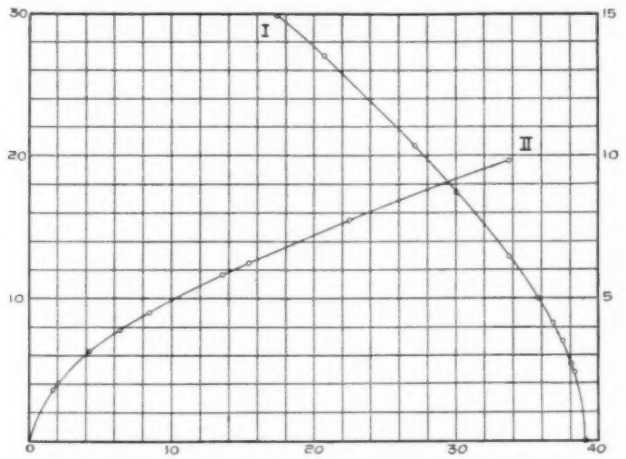

Fig. 2. I., Calibration of repulsion voltmeter for July 12. II., Calibration of Dolezalek electrometer for July 5. For I.: Abscissæ = scale reading (cm.) on scale 1 m. from mirror. Ordinates = kilo-volts (scale on left). For II.: Abscissæ = deflection (cm.) on scale 1 m. from mirror. Ordinates = volts (scale on right).

solution of sodium thio-sulphate. Readings could be made to 0.01 c.c. = .0048 mg. ozone. If recoloration of the titrated solution occurred within two hours the experiment was discarded. Professor Warburg has shown that absence of such recoloration within two hours proves that practically no nitrous oxide was present.[1]

Point and Plate Electrodes. — As a test of the apparatus the first experiments were with one plane electrode 13 cm. by 5 cm., and the other electrode having 90 pin points distributed over an equal area. Under the best conditions the yield was about 12 gr. per kilowatt hour (at the electrodes) and .04 gr. per coulomb. The current varied from 300 to 2,000 micro-amperes. As the distance

[1] Annalen der Physik, 17, 1905, p. 22. With the second type of ozonizer, the type employed in most of the experiments described in this paper, the production of nitrous oxide is much less than with a point electrode. Apparently, the more diffuse the discharge the less the production of nitrous oxide.

between the electrodes was increased the maximum current decreased, the yield per coulomb increased and per kilowatt hour decreased. In general the results obtained showed good agreement with the experiments conducted in Professor Warburg's laboratory and therefore the apparatus and methods were considered satisfactory.

Point and Point Electrodes. — Two point electrodes similar to the one above gave a very low relative efficiency, sparks occurring more readily than with point and plate electrodes. Experiment 88 of July 27 is typical.

Distance between electrodes = 2.0 cm. Gas velocity = 3 l. per min.
Current (micro-amperes) = 1,300. Dif. of Pot. = 1,500.
Yield per coulomb = .003; per kilowatt hr. = 1.1.

Plate and Plate Electrodes. — A very inefficient system, as sparks occur before the desired brush discharge is appreciable.

Gauze and Plate Electrodes. — Various copper and brass gauzes with meshes varying from 40 to 1,600 per sq. in. were tried, the edges of the electrodes being carefully turned in to avoid points. The maximum current before sparking was very low and so also was the yield of ozone. The same results were found with both electrodes gauzes.[1]

Both Electrode Plates, one bare, the other covered with a Dielectric. — The electrodes were tin plates 7.3 cm. in diameter, one covered with a glass crystallizing dish with 4 cm. sides (see Fig. 1).

Variation of Gas Velocity. — Since the yield varies also with the current observations are made with each gas velocity throughout the range of the current. The results are given in table I. Every attempted experiment was numbered and omitted numbers belonged to incomplete or unreliable experiments. *The gas velocity v is in liters per min. The potential V, in volts, the current i in micro-amperes, the mass of ozone, m, is the actual number of milligrams per minute. the yield Y_1, the number of grams per coulomb and Y_2 the number of grams per kilowatt hour. Y_2 is less than the true yield per kilowatt hour* for the power factor was never one and probably much less than one for the shorter distances. The writer hopes shortly to determine the value of the power factor under the various conditions of these experiments.

[1] Contrary to the results of Rosenberg (Elec. Rev. (London), 55, p. 807), but see Electric World, Aug. 12, 1905, p. 267.

TABLE I.

Distance between Electrodes $= d_1 = 1.00$ *cm.; between bare Electrode and Glass* $= d_2 =$ .65 *cm.; Thickness of Glass* $=$ .2 *cm.*

No.	v	V	i	m	Y_1	Y_2
52	4.5	14,700	1,100	1.26	.019	4.7
53	4.5	13,200	480	2.32	.081	24.0
54	4.5	12,000	270	2.4	.123	36.0
56	4.5	10,400	44	0	0	0
60	2.4	12,200	117	.30	.043	12.0
61	2.4	12,600	210	.92	.073	20.0
62	2.4	15,800	2,000	.96	.008	1.8
63	12.0	11,200	143	.22	.026	7.7
64	13.9	15,600	1,960	9.1	.077	17.0
65	13.9	13,100	500	3.5	.12	32.0
67	2.2	12,200	515	.71	.023	6.8
68	12.0	11,600	270	3.1	.18	57.0
69	12.9	11,600	220	1.85	.14	45.0
70	12.9	12,200	360	4.3	.20	60.0
71	4.5	12,000	158	.90	.095	29.0

The relations between yields per coulombs Y_1, current i, and gas velocity v are plotted in Fig. 3. The curves show conspicuously

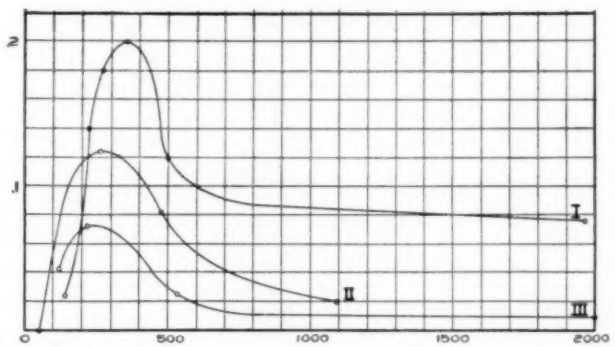

Fig. 3. Abscissæ = Micro-amperes. Ordinates = Grams per coulomb. Polar Distance = 1.0 cm. I., 13 liters of air per minute; II., 4.5 liters of air per minute; III., 2.4 liters of air per minute.

that the greater the current, the greater both the ozonizing power of the current and its deozonizing effect on the ozone already formed resulting in the maxima of the curves. The greater the gas velocity, the greater the maximum yield and the current at which this maximum occurs, and the greater the ozone density or the mass of ozone

per liter. (The latter is evident upon comparison of the second and fifth columns.) It is therefore evident that *for greatest efficiency a high gas velocity must be used.*

Upon plotting potential horizontally and current vertically the rapid increase of current at a certain potential is very evident (Fig. 4). At this point where the current commences to rapidly increase with the potential, the discharge begins to be both visible and audible and the production of ozone commences. Fig. 4 also proves

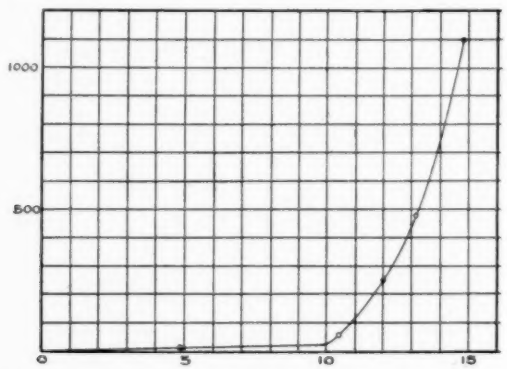

Fig. 4 Abscissæ = Kilo-volts. Ordinates = Micro-amperes. Polar Distance = 1.0 cm. Thickness of glass = .2 cm. 4.5 liters of gas per minute.

the small amount of leakage over the glass surface and the relatively small "condenser" current in the gas.

Variation of Distance.— Gas velocity = constant = 12 l. per min. One electrode = bare tin plate 7.3 cm. in diameter, the other a similar disc of tin foil cemented inside a crystallizing dish.

TABLE II.

d_1 = *Distance between Electrodes* = .60; d_2 = *Distance between bare Electrode and Glass* = .45.

No.	V	i	m	Y_1	Y_2
72	14,500	2,360	8.1	.057	14
73	14,300	2,280	8.8	.064	16
74	9,500	1,060	8.9	.14	44
75	7,300	300	1.8	.10	50
76	8,200	830	5.7	.115	55
77	6,200	560	3.7	.109	63
78	10,200	1,200	15.0	.208	73
79	11,800	1,720	13.8	.132	40
80	10,600	1,380	14.2	.173	58

TABLE III.

$d_1 = 3.20$; $d_2 = 3.05$.

No.	V	i	m	Y_1	Y_2
81	26,200	1,840	5.3	.048	6.6
83	23,800	680	4.8	.118	18.0
84	23,200	310	2.9	.16	25.0
85	22,400	180	2.6	.24	38.0
86	18,400	49	0	0	0

The results are plotted in Fig. 5. With the greater distance the air current was wider and consequently the speed of the air particles less, the volume gas velocity being the same — 12 liters per min.

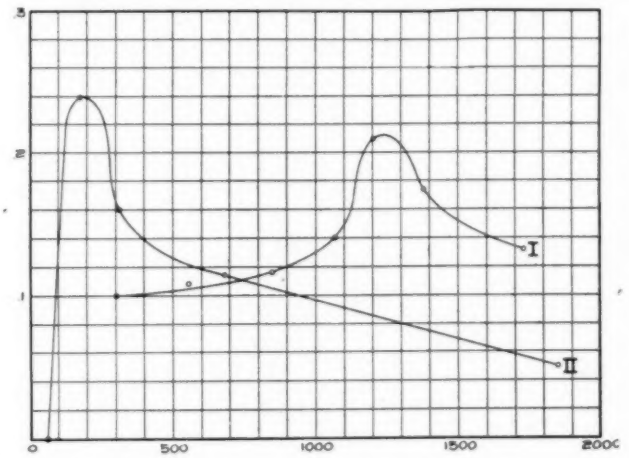

Fig. 5. Abscissæ = Micro-amperes. Ordinates = Grams of ozone per coulomb. Liters of gas per minute = 12. I., Polar Distance = .6 cm.; II., Polar Distance = 3.2 cm.

The ozone formed was therefore longer exposed to the deozonizing effect of the current and the maximum yield comes at a lower current.

Experiment 78, which represented approximately the best conditions, will be described in full.

July 17. Temp. = 27°. Bar. = 75.2. Sultry.

Sample tube = 640 c.c. Gas velocity = 12 l. per min.

$d_1 = .60$. $d_2 = .45$.

Repulsion voltmeter = 35.8 (zero = 39.4); from calibration of that day = 10,200 volts.

Dolezalek electrometer = 10.6 (zero = — 5.0) = 6.0 volts.

Non-inductive resistance = 5,000 $\therefore i$ = 1,200 micro-amperes.

$Na_2S_2O_3$ titration = 1.66 c.c. = .80 mg. O_3.

O_3 per min. = .80 × 12 ÷ .64 = 15 mg. Coulombs per min = .072. Watts = 12.2.

Yield per coulomb = .208.

Yield per kilowatt hr. = 73.

Ozone density = 1.39 gr. per cubic meter.

The above results show that if the amount of gas which flows between the electrodes is the same, the maximum yield of ozone per coulomb is approximately independent of the distance between the electrodes, but that if the distance is decreased, the current at which this maximum occurs is greater, and hence the ozone density is greater and a small distance is preferable. Would the shorter distance also be preferable if the actual velocity of the air particles was the same? A large number of experiments were made with different distances, the gas space and the volume gas velocity being adjusted so that the average velocity of the air molecules was approximately the same. The modified apparatus was not entirely satisfactory and the results were not as reliable and consistent as in the rest of the work and will not be given in detail. The results indicated that with equal velocities of the gas particles the maximum yield per coulomb was greater for the greater distance, but increased at a considerably less rate than the distance. The current for which the maximum yield occurred at the greater distance was nearly equal to the corresponding value of the current for the less distance. These results can also be deduced from a study of Figs. 3 and 5.

Effect of Width of Electrodes. — One electrode = bare tin plate 7.0 × 1.4 cm.

Other electrode = tin foil strip 7.0 × 1.4 cm. inside crystallizing dish.

d_1 = .95. d_2 = .80 cm. Gas velocity = 12 l. per min.

TABLE IV.

Greater Dimension of Electrodes Perpendicular to Gas Current.

No.	V	i	m	Y_1	Y_2
157	21,500	1,060	6.3	.10	17
159	17,500	660	7.3	.35	72
161	20,200	800	18.7	.39	70
162	22,500	980	15.3	.26	41
163	16,000	500	6.3	.21	47

TABLE V.

Greater Dimension Lengthwise to Gas Stream.

No.	V	i	m	V_1	V_2
164	22,500	1,060	4.1	.065	10
165	20,000	810	7.4	.15	27
166	17,300	590	5.3	.15	31
167	18,000	670	6.4	.16	32

These results are plotted in Fig. 6. *Narrow electrodes are evidently much more efficient*, a result expected since the ozone formed

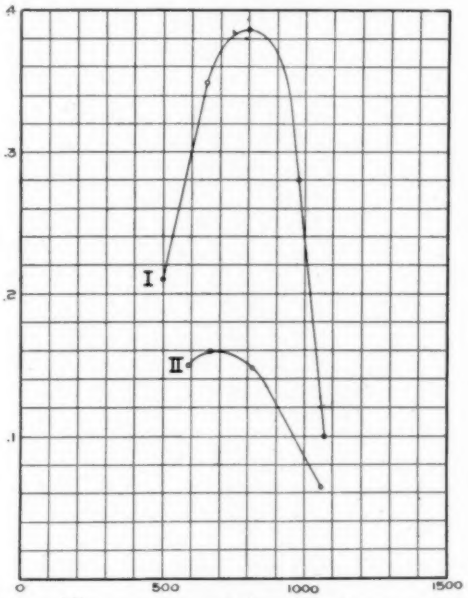

Fig. 6. Abscissæ = Micro-amperes. Ordinates = Grams per coulomb. Polar distance = .95 cm. 12 liters of air per minute. Electrodes 7.0 cm. by 1.4 cm. I., Longer dimension perpendicular to air stream. II., Longer dimensions parallel to air stream.

is exposed for less time to the current's deozonizing influence.

Influence of Dielectric. — One electrode bare, the other covered with one crystallizing dish.

$d_1 = .95$, $d_2 = .80$. Gas velocity = 12 l. per min.

TABLE VI.

No.	V	i	m	V_1	V_2
132	16,800	920	15.2	.28	61
133	15,900	780	17.4	.37	84
134	15,100	700	13.4	.32	76
136	14,000	600	9.3	.26	67

Experiment 133 will be given in full.

August 9. Temp. = 24°, Bar. = 75.8.

Sample tube = 680 c.c. Gas velocity = 12 l. per min. $d_1 = .95$. $d_2 = .80$.

Repulsion voltmeter = 30.9 (zero = 39) = 15,900 volts.

Dolezalek electrometer = 21.7 (zero = − 6.8) = 7.8 volts.

Non-inductive resistance = 10,000 ohms, hence $i = 780$ micro-amperes.

$Na_2S_2O_3$ titration = 2.06 c.c. = .99 mg. ozone.

Ozone per minute = .99 × 12 ÷ .68 = 17.5 mg.

Coulombs per minute = .047. Yield per coulomb = .37.

Watts = 12.4. Yield per kilowatt hour = 84.

Ozone density = 1.46 gr. per cubic meter.

One electrode plain, the other covered with two crystallizing dishes.

$d_1 = 1.2$. $d_2 = .80$. Gas velocity = 12 l. per min.

TABLE VII.

No.	V	i	m	Y_1	Y_2
122	17,500	450	5.7	.21	44
123	19,200	660	9.9	.25	47
124	21,400	860	21.2	.41	68
126	22,800	1,020	12.8	.21	33
128	21,500	840	16.6	.31	52
129	23,400	1,120	12.1	.18	28
130	19,400	690	12.4	.30	56
131	20,400	790	20.9	.44	65

Both Electrodes Covered with Glass. — Both electrodes consist of tin foil on the inside of glass crystallizing dishes.

$d_1 = 1.0$, $d_2 = .85$. Gas vel. = 12 l. per min.

TABLE VIII.

No.	V	i	m	Y_1	Y_2
95	28,000	1,280	11.2	.13	17
98	13,700	232	1.8	.13	35
99	19,700	590	5.6	.16	29
100	24,000	820	7.9	.16	24
101	18,000	440	3.6	.14	28
103	30,200	1,240	11.2	.15	18
104	22,600	680	5.8	.14	22
107	31,400	1,100	11.8	.18	21
108	26,000	870	8.3	.16	22

The relations between yield per coulomb and current are plotted in Fig. 7.

Comparing these different results, it is evident that the thickness (and hence the nature) of the dielectric has practically no influence on the yield per coulomb but that if both are covered with dielectric the yield per coulomb is less (and the apparent resistance is greater). Also, the less the dielectric the lower the required

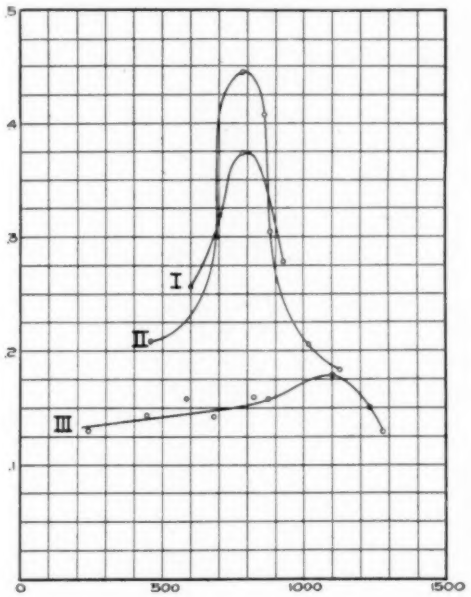

Fig. 7. Abscissæ = Micro-amperes. Ordinates = Grams per coulomb. Polar distance = about 1 cm. 12 liters of air per minute. I., One electrode bare, the other covered with single glass. II., One electrode bare, the other covered with double glass. III., Both electrodes covered with glass.

potential and the greater the yield per kilowatt hour. Therefore *for greatest commercial efficiency*, there should be a *thin dielectric of high dielectric strength in the gas space between the electrodes.*

When the potential is sufficient to make the air conducting, the air is most luminous near the electrodes. Professor Warburg[1] has shown that with point and plate electrodes, luminosity and the production of ozone are very intimately connected. It is, therefore, natural that we find more ozone produced near the electrodes in this type of ozonizer.

[1] Ann. der Physik, 17, 1985, p. 1.

Comparing the best yield per kilowatt hour with point and plate electrodes, 27 grams with points positive and 13 grams with points negative or alternating, *with the yield of over 70 under the best conditions with alternating current and the electrodes separated by a dielectric* (see Tables II., IV. and VI.) *it is evident that the latter system is by far the more efficient.* The actual yield is considerably over 70 since the power factor has been assumed as unity.

Conclusions. — These experiments upon the electrical production of ozone have chiefly shown three things; first, the superiority of the silent discharge obtained with an alternating current and the interposition of dielectric between the electrodes, over that obtained with a point electrode; second, the marked deozonizing effect of the current and how to reduce this influence, and third, the ideal dielectric. [1]

I wish to thank Professor Warburg for the hospitality of his private laboratory where I began the study of the electrical production of ozone under his guidance and Prof. H. B. Smith for very kindly placing at my service the high potential apparatus of the Department of Electrical Engineering, of the Worcester Polytechnic Institute.

SALISBURY LABORATORIES,
WORCESTER POLYTECHNIC INSTITUTE,
WORCESTER, December, 1905.

[1] [An ozonizer has been constructed embodying the results of these experiments and in preliminary trials shows very high efficiency. The electrodes are straight, parallel, nickel-plated wires, all in the same plane, alternate wires projecting on each side and being joined to the external electrode. Perpendicular to the plane of the wires and *midway between each pair of wires* is a flat plate of dielectric, sufficiently wide to prevent direct discharge between the wires. The shape of the dielectric being the simplest possible, the danger from breakage is a minimum and the choice of dielectrics is greatly increased. Glass and fiber have proved very satisfactory. Hard rubber is apparently acted upon by the ozone and mica gives an irregular discharge. March, 1906.]

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE THIRTY-FIRST MEETING.

A REGULAR meeting of the Physical Society was held in Fayerweather Hall, Columbia University, New York City, on Saturday, February 24, 1906. President Barus presided.

On motion the president, the secretary and E. B. Rosa were made a committee to prepare a memorial to Congress urging the passage of the pending bill which provides for the use of the metric system in all the government departments.

On motion a committee was appointed consisting of A. G. Webster (chairman), M. I. Pupin and P. C. Hewitt, to consider the practicability of securing for the Physical Society an endowment fund, the income of which shall be available to meet the expenses of committees appointed by the Society to investigate and report on special topics of importance.

The following papers were read:

1. A Direct-Recording Magnetic Declinometer. W. G. CADY.

2. A Machine for Compounding Sine Curves. W. G. CADY.

3. The Damping of a Ballistic Galvanometer. (Read by title.) A. W. SMITH.

4. Further Experiments on the Decay of Phosphorescence in Sidot Blende. E. L. NICHOLS and ERNEST MERRITT.

5. The Decay of Phosphorescence in a Certain Specimen of Willemite. E. L. NICHOLS and ERNEST MERRITT.

6. The Gray Absolute Electrodynamometer. E. B. ROSA.

7. On the Relative Proportion of the Total X-ray Activity of Radioactive Minerals due to the Separate Radioactive Constituents. B. B. BOLTWOOD.

8. The Radioactivity of Thorium. H. M. DADOURIAN.

9. Nucleation and Ionization in CO_2 and Coal Gas. CARL BARUS.

10. Temperature Records of Nocturnal Radiation. H. T. BARNES.

11. On the Possible Separation of Electric Charges by Centrifugal Accelerations. E. F. NICHOLS.

The spring meeting of the society will be held in Washington.

ERNEST MERRITT,
Secretary.

TREASURER'S REPORT FOR THE YEAR 1905.

RECEIPTS.

Balance from 1904	$1,625.12	
Interest on balance	56.88	
Arrears of dues	15.00	
Life membership fees, three	150.00	
Initiation fees, twenty	60.00	
Refund on Nomenclature Committee	17.60	
Annual dues for 1905	1,295.00	$3,219.60

DISBURSEMENTS.

Physical Review, 247	$ 741.00	
Science abstracts, 284	426.00	
Andrus and Church, Printing, etc	128.00	
Office of Secretary	142.40	
Office of Treasurer	21.40	
Drafts and collections	3.50	
Incidental printing	14.47	$1,477.07
Balance carried to 1906		1,742.53
		$3,219.60
Total annual outlay		$1,477.07
Interest on fund	$ 56.88	
Annual dues	1,295.00	
	1,351.88	
APPARENT DEFICIT	125.19	1,477.07

THERMOELECTRIC HETEROGENEITY IN CERTAIN ALLOYS, ESPECIALLY GERMAN-SILVER.[1]

BY EDWIN H. HALL, L. L. CAMPBELL AND S. B. SERVISS.

IN calibrating thermo-electric couples made of annealed german-silver with copper for the temperature region 100° to 218°, using a temperature interval not far from 40°, the authors found the electromotive force, in the case of some couples, to vary as much as two or three per cent. of itself when the junction which had been the hotter became the colder and *vice versa*. The german-silver wires were about 0.02 cm. in diameter and about 150 cm. long. A part some 45 cm. long near the middle of each german-silver wire was, in these experiments, outside the heating vessels, and at first no care was taken to keep this part warm, so that steep gradients of temperature existed in the german-silver wire just outside the entrance to each vessel. It was at first thought that local peculiarities of this wire due to accidental bending or stretching after the an-

[1] Abstract of a paper presented at the meeting of the Physical Society held on Dec. 29–30, 1905.

nealing might, if these peculiarities happened to come at places where the temperature gradient was steep, cause the changes observed on reversal of the temperature interval of the junctions. Experiment seemed to show, however, that these peculiarities could not reasonably be made to account for all of the difference of electromotive force observed on this reversal.

Further experiments, made by touching with the sharp edge of a lump of ice various points 1 cm. apart on long straight pieces of german-silver wire exposed to air at a temperature of 18° or 20° centigrade, gave perceptible electromotive forces, some of which were in one direction and some in the other direction, about twenty changes of sign occurring in a distance of 50 cm. along the wire. Annealing a wire, by heating to incandescence for a few seconds in air, was found to increase its thermo-electric heterogeneity. Permanent stretching of a wire 10 per cent. left the local thermo-electric peculiarities almost unchanged in magnitude and in distribution. Reannealing a wire after such a stretching again increased these local peculiarities and changed their distribution. The greatest electromotive force observed on touching a german-silver wire with ice was about $\frac{1}{500}$ part of that which would have been produced by touching a junction of copper and german-silver. The heterogeneity thus found in straight recently annealed wire is great enough to be a possible source of serious error in cases where a copper-german-silver couple is used to measure a small difference between two temperatures much above the temperature of the room, if the middle part of the german-silver wire is freely exposed to the air. In later calibration experiments the difference of electromotive force found on reversal of the temperature interval of the junctions was greatly diminished by protecting the middle parts of the german-silver wires with asbestos fiber, so that, being near the heating vessels, they were raised to a temperature not far below that of the cooler vessel.

A manganin wire, tested by touching at various points with ice, behaved very much as german-silver wire did. A constantin wire showed local differences, but these were much less than in german-silver or in manganin.

The Optical Properties of Carbon.[1]

By Herbert A. Clark.

An anomaly in the dispersion and in the absorbing and radiating powers of carbon has been found by Wood and E. L. Nichols. In view of this fact, it has seemed worth while to obtain data regarding the reflection as well as the absorption and dispersion, all from the same specimen, of carbon deposited in various ways.

[1] Abstract of a paper presented at the meeting of the Physical Society held on Dec. 29–30, 1905.

In this work, transparent films were used, some deposited in vacuo and some on the inside of an electric lamp globe. Of the former, the reflection, refraction, and transmission were obtained quantitatively throughout the visible spectrum; and the transmission qualitatively in the ultraviolet. Of the latter films, the transmission and the direction of the refractive index curve were obtained in the visible spectrum. As is to be expected from the observations of others upon the electrical properties of thin films, the optical properties vary markedly with the manner and conditions of deposit.

METHODS OF SOIL HYGROMETRY.[1]

BY E. BUCKINGHAM.

AFTER a brief mention of the importance in agricultural investigations of having a good method for determining the water content of the soil at any given depth, and a statement of the merits and defects of the gravimetric and electrolytic methods now in use, the paper goes on to state the general principles on which any successful method must be based.

It is necessary to select some physical property of the soil which may be conveniently and accurately measured without disturbing the soil; and the property must be such that to every measured value of this property there corresponds one and only one value of the water content of the soil. The property must vary sufficiently with the water content of the soil, and must not depend on the variable concentration of the substances dissolved in the soil moisture.

The index of refraction for short electrical waves appears to satisfy these requirements reasonably well. Experiments by L. J. Briggs and the writer, using Drude's method, with the soil in the end condenser and a wave-length of from 50 cm. to 200 cm., showed that the specific inductive capacity of the soil does vary sufficiently with the water content and is independent of the concentration of the soil solution, up to such concentrations as occur under natural conditions in the soil. Further experiments were made similar to Hertz's original experiment with the wire rectangle,[2] and to the experiments of Rubens and Arons.[3] Waves from an oscillator enter a divided circuit and, after traversing the two arms, meet at a spark micrometer where the sparking is a minimum if the same time is required for the waves to traverse each arm. If one

[1] Abstract of a paper presented at the meeting of the Physical Society held on Dec. 29–30, 1905.

[2] Wied. Ann. **31**, 421, 1887.

[3] Wied. Ann. **42**, 581; **44**, 206. 1891.

arm of the circuit is led through the ground, the point at which the waves must be introduced in order to give a minimum of sparking at the spark micrometer, varies with the wetness of the soil, and by gravimetric calibration the readings of the instrument may be interpreted in terms of the percentage of water in the soil surrounding the soil arm of the circuit. It is hoped to extend these experiments, which only have a preliminary character, and to develop on these lines a practical method of soil hygrometry. Diagrams of the instrumental arrangements were shown, together with a graphical representation of results obtained during June, 1905, in the loam soil of a flower bed.

A Direct-Recording Magnetic Declinometer.[1]

By W. G. Cady.

A PRELIMINARY paper on this instrument was published in *Terrestrial Magnetism* for June, 1904. Since then one declinometer of this type has been constructed at Wesleyan for the Dept. of Terr. Mag. of the Carnegie Institution and sent to the Solar Observatory at Mt. Wilson, Cal. A second instrument, also intended for the Carnegie Institution, is now nearing completion.

The motion of a magnetic needle is transmitted through a delicate suspended lever to a glass pen, which prints a dot once a minute on a strip of paper. The paper is advanced and the printing accomplished automatically by means of clockwork. Also, if the magnet changes its direction by more than a prescribed amount, an electric alarm rings. Due allowance is here made for the normal course of diurnal variation.

A fixed pen traces a base-line near one edge of the paper. To determine the sensitiveness, a telescope, scale, and deflecting magnet are provided. The sensitiveness can be varied at will; good records are obtained with the scale-value as small as 1.5 minutes of arc per millimeter.

A Machine for Compounding Sine Curves.[1]

By W. G. Cady.

A PENCIL moved up and down by a train of gear wheels pressed against a vertical sheet of paper, which is drawn along horizontally by means of a rack and pinion. The same shaft that turns the wheels also advances the paper. By means of reduction gearing and various

[1] Abstract of a paper presented at the meeting of the Physical Society held on Feb. 24, 1906.

adjustments, a fundamental sine curve with a period of 48 cm. can be drawn alone, or compounded with its second, third or fifth harmonic, any desired amplitude and phase relations being possible. The machine itself was shown, together with various sample curves.

DAMPING OF A BALLISTIC GALVANOMETER.

BY ARTHUR W. SMITH.

THE equation of the ballistic galvanometer is

$$Q = \frac{H}{G}\frac{T}{\pi}\theta = \frac{H}{G}\frac{T}{\pi}\theta_1\left(1 + \frac{\lambda}{2}\right),$$

where θ denotes the virtual deflection which would be obtained if there were no damping. The actual deflection, θ_1, is less than θ, the familiar relation being $\theta = \theta_1(1 + \lambda/2 +)$. λ is the logarithmic decrement, *i. e.*, the natural logarithm of the ratio of one amplitude to the next.

A more simple method of determining the damping factor is the following: For brevity let k denote this factor. By definition, $\theta = k\theta_1$. Similarly $\theta_1 = k\theta_2$, where θ_2 is the virtual deflection at the end of the second half amplitude and when the needle is passing its position of rest.

In other words, θ_2 is the deflection which would be obtained if damping should suddenly cease at the end of the second half amplitude. The actual deflection, θ_3, is less than this, or $\theta_2 = k\theta_3$. In the same way, $\theta_3 = k\theta_4$ and $\theta_4 = k\theta_5$, θ_5 being the next deflection in the same direction as θ_1. Hence $\theta_1 = k^4\theta_5$, and $\theta = (\theta_1/\theta_5)^{\frac{1}{4}}\theta_1$. The complete equation then becomes

$$Q = \frac{H}{G}\frac{T}{\pi}\theta_1\left(\frac{\theta_1}{\theta_5}\right)^{\frac{1}{4}},$$

which is much more simple and direct than the usual method of considering the "logarithmic decrement" and obtaining k in the form of an infinite series.

TEMPERATURE RECORDS OF NOCTURNAL RADIATION.[1]

BY H. T. BARNES.

ON account of the great cold of the Canadian winter together with the extreme dryness of the atmosphere it was considered of interest to obtain some record of the copious radiation that takes place from the surface into space during the night time.

[1] Abstract of a paper presented at the meeting of the Physical Society held on Feb. 24, 1906.

Until more satisfactory apparatus could be obtained for permanently carrying out the work, the electric recorder was used, which is in use at the McGill College Observatory for giving the difference in temperature at different altitudes, and which was described at the last meeting of the Physical Society by Professor McLeod and the author.

The high level thermometer was brought down and connected in the circuit at the observatory beside the low level instrument, and temperature traces taken on several clear nights with one thermometer exposed to the sky and the other under cover.

A considerable divergence from the zero line was obtained which varied with the clearness of the atmosphere.

At the present time a special recorder is being fitted up with special thermometers and it is the author's intention to continue the work for the rest of the winter, and at the same time to obtain if possible the absorptive power of some materials for the long heat waves radiated from the earth at a low temperature.

That the radiation is considerable, is shown by the abundant formation of anchor or ground ice at the bottom of quite deep rivers and streams which are flowing too swiftly to allow surface ice to form. This ice is dependent on the clearness of the sky and never forms under surface ice.

McDONALD PHYSICS BUILDING,
McGILL UNIVERSITY, February 19, 1906.

THE RADIO-ACTIVITY OF THORIUM.[1]

BY H. M. DADOURIAN.

IT has been claimed by several experimenters that the radio-activity of different preparations of thorium is not the same, in fact, that it is possible to obtain, from certain sources, thorium which is entirely inactive.

In view of these facts and of the doubts which have been raised as to the elementary character of thorium it was deemed desirable to determine the quantitative relation between the thorium activity of various minerals and separated salts, and their content of thorium.

The method used was based upon the measurement of the activity of the material deposited upon a cathode exposed to the emanation from solutions of these minerals and salts. The slower decay of the deposit due to the thorium emanation made it possible to separate it from the deposits due to radium and actinium. The method proved to be capable of giving accurate quantitative results.

[1] Abstract of a paper presented at the meeting of the Physical Society held on Feb. 24, 1906.

It was found that the thorium activity of thorite and thorianite taken as natural minerals was proportional to the amount of thorium contained in these minerals, while thorium nitrate from North Carolina and Brazilian monazites prepared by the Welsbach Light Company had a specific thorium activity only half as large.

To make this certain Dr. B. B. Boltwood, to whom the writer is indebted for all the minerals and salts used in these experiments, separated the thorium from a few grams of North Carolina monazite and converted it into a nitrate. The specific thorium activity of this preparation was found to be equal to the specific thorium activity of thorite and thorianite.

These results show that the radio-activity of thorium, and consequently the radio-thorium in a mineral, is proportional to the quantity of thorium present in the mineral, further, that radio-thorium is a disintegration product of thorium.

The fact that commercially prepared thorium salts have lower specific thorium activity leads to the conclusion that about half of the equilibrium quantity of radio-thorium is removed from these salts in the chemical process of their preparation.

The results of these experiments strongly indicate the elementary character of thorium itself.

In conclusion I wish to express my hearty thanks to Professor H. A. Bumstead for suggesting these experiments and for the interest he has shown during the progress of the work.

THE NUCLEATION AND IONIZATION OF CARBON DIOXIDE AND COAL GAS.[1]

BY CARL BARUS.

IN these experiments I have used the apparatus with which I obtained the data in case of dust-free air, for CO_2 and coal gas, finding the nucleation for these gases both in the non-energized and in a typically energized state. The results in both investigations are suggestive in character. CO_2 behaves in a way closely resembling air (energized or not), but in such a way that a given corona appears in CO_2 at a pressure difference about 5.5 cm. higher than in case of air. In other words the behavior is as if the nuclei of CO_2 were throughout smaller. It is to be noticed, however, that the heat ratio γ is smaller for CO_2 than for air which would in part account for this result.

Coal gas needs more detailed discussion, but behaves in general like CO_2.

[1] Abstract of a paper presented at the meeting of the Physical Society held on Feb. 24, 1906.

NEW BOOKS.

Die Kathodenstrahlen. By G. C. SCHMIDT. 8vo, pp. vii + 120. Braunschweig, Vieweg und Sohn, 1904.

Electromagnetische Schwingungen und Wellen. By JOSEF RITTER VON GEITLER. 8vo, pp. viii + 154. Braunschweig, Vieweg und Sohn. 1905.

Die Physikalischen Eigenschaften der Seen. By OTTO FREIHERR VON UND ZU AUFSESS. 8vo, pp. x + 120. Braunschweig, Vieweg und Sohn, 1905.

These interesting and useful little books form part of a series of semi-popular monographs on scientific and mathematical subjects, the publication of which, under the general title "Die Wissenschaft," was begun two years ago. The place of honor as first of the series was given to a German translation of Madame Curie's dissertation on Radioactive Substances. The plan and purpose of the series are explained in the following extract from the publisher's announcement:

"It is becoming more difficult every year to follow the advances that are being made in the mathematical and natural sciences. It is true that numerous reference periodicals report the results of the more recent investigations with more or less promptness, but without systematizing and unifying these results. The progress made in the various branches of science can be readily followed, however, only when comprehensive résumés, each dealing with some special topic, appear at rather frequent intervals. Such résumés would serve also to give the specialist a glimpse into those fields of scientific activity which are related to his specialty. Considerations of this kind have led in France to the publication of the 'Scientia' series. In Germany the collection of monographs on scientific and mathematical subjects which is to appear under the title 'Die Wissenschaft' is intended to serve the same purpose. The treatment is not intended to be 'popular' in the ordinary sense in which the word is used, since not only the results of general interest will be presented, but also the experiments and the theoretical considerations which have led to the results. . . ."

It is scarcely to be expected that these monographs will be very generally read in this country outside of scientific circles, for the treatment is more thorough than is usual in our popular scientific books. But for those having the requisite knowledge of German, and who desire

something more than the superficial accounts of scientific work that are so common with us, the collection will be quite welcome. For physicists who wish to keep track of the progress in branches related to their own, but who cannot spare the time needed for the consultation of the original articles, "Die Wissenschaft" collection will certainly be found extremely useful.

The monograph by Professor Schmidt on the Cathode Rays is a very readable and reasonably complete account of the development of this important subject down to the year 1904. Not only the ordinary cathode rays of the vacuum tube but also those developed in other ways are considered; for example the rays produced at the surface of an incandescent body by the action of ultra-violet light, and the β-rays of radium. The book also contains chapters on canal rays, the Zeeman effect, and apparent mass. The significance of the results in their bearing upon the electron theory is accentuated. A systematic arrangement of the material in chapters in part makes up for the unfortunate lack of an index, while references to original articles, although by no means complete, include the most important work up to the time of publication.

Numerous books of a popular and semi-popular character dealing with electric oscillations and electric waves have appeared in recent years, and have treated the subject in a variety of different ways. In some cases it is the experimental side of the subject that has been thrown into the foreground; in others especial prominence has been given to the bearing of the work of Hertz upon electrical and optical theories; while in many instances the purely scientific side of the subject has been subordinated to the applications of electric waves in wireless telegraphy. If only one book on the subject is to be read, it is probable that either one of several books that might be mentioned would be found more satisfactory than that of von Geitler. But for one wishing to go into the subject more thoroughly this little monograph will be found very useful. The treatment is often so brief as to be in itself quite inadequate. But on the other hand the book contains a large amount of material which it would be difficult to find elsewhere without an extended search of the literature, and the value of the book is greatly increased by the unusually complete references to original papers. As a book of reference especially it will take a position that has not before been adequately filled.

In the "Physical Properties of Lakes," by von Aufsess, we have an interesting presentation of an unusual subject. I think that the physicist often experiences a certain feeling of envy when he sees how readily the botanist or the mineralogist is able to combine a summer outing or an interesting journey with more or less serious scientific work. To some extent the physicist is able to do this also, as is evidenced by Tyndall's study of the Alpine glaciers, and by the work of Elster and Geitel

on atmpospheric ionization. But such cases are not usual. The little book by Freiherr von Aufsess will give to the physicist who loves outdoor life an added interest in any lake that he may encounter in his travels, and will help to explain some of the phenomena that must have puzzled every one who has spent any time near a large body of water.

The book is divided into chapters according to the branch of physics in which the phenomena considered naturally fall: Mechanics, Sound, Light, and Heat. Personally the reviewer has found the most interesting chapters to be those dealing respectively with waves and with the color of lakes. The treatment is often not as complete as might be desired; in many cases the problems have doubtless not yet been fully solved. The book is not to be compared in interest with the writings of Tyndall on the Alps, since the narrative element is lacking; but it forms one of a class of books on physics whose number is as yet far too small.

ERNEST MERRITT.

Populäre Schriften. By LUDWIG BOLTZMANN. 8vo., pp. vii + 440. Leipzig, Barth, 1905.

Those who are familiar with the clear and pleasing style which Boltzmann can adopt when he enters the field of semipopular writing will welcome the appearance of this collection. It contains twenty-three addresses or magazine articles, dealing with a great variety of subjects, chiefly, however, such as are closely connected with physics. The following titles will give an indication of the nature of the topics considered: "Die Methoden der theoretischen Physik"; "Ueber Maxwell's Elektrizitätstheorie," especially interesting because of its original appearance, in 1873, before the theory had reached its present secure position; "Der Zweite Hauptsatz der Mechanischen Wärmetheorie"; "Ueber Luftschiffahrt"; "Josef Stefan" "Zur Energetik"; "Ueber die Unentbehrlichkeit der Atomistik in der Naturwissenschaft"; "Ueber die Prinzipien der Mechanik": "Ueber eine These Schopenhauers."

Among the papers which do not deal with scientific subjects the "Reise eines deutschen Professors ins Eldorado" will probably arouse the most interest among American readers, since it describes the author's visit to this country in the summer of 1904, when he delivered a course of lectures at the University of California. While possessing a certain cynical humor this article seems out of place in a collection of scientific articles. The book would have gained in dignity by its omission.

E. M.

Die Moderne Theorie der physikalischen Erscheinungen. (Radioaktivität, Ionen, Elektronen.) By A. RIGHI. German translation by B. DERSAU. 8vo, pp. 152. Leipzig, Barth, 1905.

La théorie moderne des phénomènes physiques : radioactivité, ions, électrons. By A. RIGHI. French translation by E. NÉCULCÉA. Preface by G. LIPPMANN. 8vo, pp. 126. Paris "L'Éclairage Électrique," 1906.

Trowbridge's English translation of Righi's interesting little book has already been referred to in these pages.[1] The appearance of the German and French translations gives evidence of the general favor with which the book has been received.

[1] PHYSICAL REVIEW, Vol. XXI., p. 205, September, 1905.